PB-221 486

DYESTUFF COLOR REMOVAL BY IONIZING RADIATION AND CHEMICAL OXIDATION

T. F. Craft, et al

Georgia Institute of Technology

Prepared for:

Environmental Protection Agency

March 1973

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

EPA-R2-73-048
March 1973

W73_11329

PB 221 486
Environmental Protection Technology Series

Dyestuff Color Removal by Ionizing Radiation and Chemical Oxidation

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. Department of Commerce
Springfield VA 22151

Office of Research and Monitoring
U.S. Environmental Protection Agency
Washington, D.C. 20460

126

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Monitoring, Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

1. Report No. 2. W73-11329

Dyestuff Color Removal By Ionizing Radiation and Chemical Oxidation,

5. Report Date

8. Performing Organization Report No.

Craft, T. F.
Eichholz, G. G.

EPA Project 12090 FZB

Engineering Experiment Station,
Georgia Institute of Technology,
Atlanta, Georgia

13. Type of Report and Period Covered

~~Environmental Protection Agency~~

Environmental Protection Agency, Technology Series report number, EPA-R2-73-048, March 1973. 118p, 66 fig, 2 tab, 32 ref

The effects of a combined radiation-oxidation process on solutions of textile dyes have been studied. ~~It was found that~~ the combined treatment with gamma radiation and chlorine causes more decolorization than the effect of the two components when they are applied individually. Several chemical classes of dyes were tested, including anthraquinone, azo, metallized azo, sulfur, stilbene, and triphenylmethane dyes. At a concentration of 0.25 g/l the transmittance at the wave-length of maximum absorbance of dye solutions is greatly increased by treatment with a radiation dose of 60 kR plus 75 ppm chlorine. Non-optimized cost estimates indicate $0.31/1000 gal. for design treatment, with normal operating costs potentially lower.

Although the major benefit from this treatment will be removal of color, some reduction of chemical oxygen demand will occur, and possibly some reduction in the biochemical oxygen demand. (EPA)

17a. Descriptors

Dyes*, Gamma Rays*, Oxidation, Wastewater Treatment, Industrial Wastes, Color

17b. Identifiers

Dye industry Wastes, Textile Finishing Wastes*, Gamma Radiation, Chemical Oxidation, *Color removal

17c. COWRR Field & Group

05B, 05D

73-048
Copy available from GPO Sup Doc as EP 1.23/2:, $2.10 ; microfiche 22[illegible]. $0.95.

19. Security Class (Report)

20. Security Class (Page)

21. No. of Pages

22. Price

Send To:
WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U S DEPARTMENT OF THE INTERIOR
WASHINGTON D C 20240

G. G. Eichholz | Georgia Institute of Technology

EPA-R2-73-048
March 1973

DYESTUFF COLOR REMOVAL BY IONIZING RADIATION AND CHEMICAL OXIDATION

By

T. F. Craft
G. G. Eichholz

Project 12090 FZB

Project Officer

Edmond P. Lomasney
Region IV - EPA
1421 Peachtree Street
Atlanta, Georgia 30309

Prepared for

OFFICE OF RESEARCH AND MONITORING
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402
Price $2.10 domestic postpaid or $1.75 GPO Bookstore

12

EPA Review Notice

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

The effects of a combined radiation-oxidation process on solutions of textile dyes have been studied. It was found that the combined treatment with gamma radiation and chlorine causes more decolorization than the effect of the two components when they are applied individually. Several chemical classes of dyes were tested, including anthraquinone, azo, metallized azo, sulfur, stilbene, and triphenylmethane dyes. At a concentration of 0.25 g/ℓ the transmittance at the wavelength of maximum absorbance of dye solutions is greatly increased by treatment with a radiation dose of 60 kR plus 75 ppm chlorine. Non-optimized cost estimates indicate $0.31/1000 gal. for design treatment, with normal operating costs potentially lower.

Although the major benefit from this treatment will be removal of color, some reduction of chemical oxygen demand will occur, and possibly some reduction in the biochemical oxygen demand.

This report is submitted in fulfillment of Project 12090 FZB between the Office of Research and Monitoring/Environmental Protection Agency and the Georgia Institute of Technology.

Keywords: Dye wastes, textile wastes, gamma radiation, chemical oxidation, industrial waste treatment

CONTENTS

Section		Page
I	Conclusions	1
II	Recommendations	3
III	Experimental Details	5
	Radiation Sources	
	Procedure	
V	Test Results	13
	Comparison of Oxidants	
	Treatment of Dye Solutions	
	Anthraquinone Dyes	
	Azo Dyes	
	Metallized Azo Dyes	
	Sulfur Dyes	
	Triphenylmethane Dyes	
	Dyes of Other Chemical Types	
	Commercial Dye Wastes	
	Effect of pH on Decolorization of Dye Solutions	
	Biochemical Oxygen Demand of Dye Solutions	
	Chemical Oxygen Demand of Dye Solutions	
	Effect of Radiation Dose Rate	
	Preliminary Cost Evaluation	
VI	Acknowledgments	31
VII	References	33
VIII	Appendix -- A. Graphical Presentation of Data	37
	B. Design Study for a Reactor Loop Irradiator	103

Preceding page blank

FIGURES

		PAGE
1	TRANSMITTANCE CURVES FOR ACID YELLOW 40 AT 0.125 g/ℓ	38
2	TRANSMITTANCE CURVES FOR DISPERSE VIOLET 18	39
3	TRANSMITTANCE CURVES FOR ACID BLUE 23 WITH 40 ppm CHLORINE	40
4	TRANSMITTANCE CURVES FOR ACID BLUE 23 WITH 80 ppm CHLORINE	41
5	TRANSMITTANCE CURVES FOR ACID BLUE 23 WITH 160 ppm CHLORINE	42
6	TRANSMITTANCE CURVES FOR NYLOSAN BLUE WITH 80 ppm CHLORINE	43
7	TRANSMITTANCE CURVES FOR NYLOSAN BLUE WITH 160 ppm CHLORINE	44
8	TRANSMITTANCE CURVES FOR ACID VIOLET 48 WITH 80 ppm CHLORINE	45
9	TRANSMITTANCE CURVES FOR ACID VIOLET 48 WITH 160 ppm CHLORINE	46
10	TRANSMITTANCE CURVES FOR DISPERSE BLUE 7	47
11	TRANSMITTANCE CURVES FOR DISPERSE VIOLET 4 WITH 80 ppm CHLORINE (METHANOL)	48
12	TRANSMITTANCE CURVES FOR DISPERSE VIOLET 4 WITH 80 ppm CHLORINE (ETHANOL)	49
13	TRANSMITTANCE CURVES FOR DISPERSE VIOLET 4 WITH 160 ppm CHLORINE (ETHANOL)	50
14	TRANSMITTANCE CURVES FOR VAT BLUE 6	51
15	TRANSMITTANCE CURVES FOR DISPERSE BLUE 73 WITH 40 ppm CHLORINE	52

FIGURES (Continued)

		PAGE
16	TRANSMITTANCE CURVES FOR DISPERSE BLUE 73 WITH 80 ppm CHLORINE	53
17	TRANSMITTANCE CURVES FOR DISPERSE BLUE 73 WITH 160 ppm CHLORINE	54
18	TRANSMITTANCE CURVES FOR DISPERSE BLUE 73 WITH 40, 80, 160 ppm CHLORINE	55
19	TRANSMITTANCE CURVES FOR LATYL CERISE Y WITH 40 ppm CHLORINE	56
20	TRANSMITTANCE CURVES FOR LATYL CERISE Y WITH 80 ppm CHLORINE	57
21	TRANSMITTANCE CURVES FOR LATYL CERISE Y WITH 160 ppm CHLORINE	58
22	TRANSMITTANCE CURVES FOR ACID YELLOW 34	59
23	TRANSMITTANCE CURVES FOR ACID YELLOW 40 WITH 160 ppm CHLORINE	60
24	TRANSMITTANCE CURVES FOR ACID RED 151 WITH 80 ppm CHLORINE	61
25	TRANSMITTANCE CURVES FOR ACID RED 151 WITH 160 ppm CHLORINE	62
26	TRANSMITTANCE CURVES FOR ACID RED 337 WITH 80 ppm CHLORINE	63
27	TRANSMITTANCE CURVES FOR ACID RED 337 WITH 160 ppm CHLORINE	64
28	TRANSMITTANCE CURVES FOR ACID BLUE 158 WITH 40 ppm CHLORINE	65
29	TRANSMITTANCE CURVES FOR ACID BLUE 158 WITH 80 ppm CHLORINE	66
30	TRANSMITTANCE CURVES FOR ACID BLUE 158 WITH 160 ppm CHLORINE	67
31	TRANSMITTANCE CURVES FOR DISPERSE YELLOW 23	68
32	TRANSMITTANCE CURVES FOR ACID YELLOW 151	69

FIGURES (Continued)

		PAGE
33	TRANSMITTANCE CURVES FOR ACID YELLOW 152	70
34	TRANSMITTANCE CURVES FOR ACID ORANGE 86 WITH 80 ppm CHLORINE	71
35	TRANSMITTANCE CURVES FOR ACID BLACK 107 WITH 80 ppm CHLORINE	72
36	TRANSMITTANCE CURVES FOR ACID BLACK 107 WITH 160 ppm CHLORINE	73
37	TRANSMITTANCE CURVES FOR CALCOFAST NEUTRAL RED 3GL	74
38	TRANSMITTANCE CURVES FOR SULFUR BROWN 14	75
39	TRANSMITTANCE CURVES FOR SULFUR BROWN 14 AND DENIVAT BLUE 57	76
40	TRANSMITTANCE CURVES FOR DENIVAT BLUE 57 WITH 40 ppm CHLORINE	77
41	TRANSMITTANCE CURVES FOR DENIVAT BLUE 57 WITH 80 ppm CHLORINE	78
42	TRANSMITTANCE CURVES FOR DENIVAT BLUE 57 WITH 160 ppm CHLORINE	79
43	TRANSMITTANCE CURVES FOR DENIVAT BLUE 57 FOR VARIOUS RADIATION DOSES	80
44	TRANSMITTANCE CURVES FOR ACID BLUE 83 WITH 40 ppm CHLORINE	81
45	TRANSMITTANCE CURVES FOR ACID BLUE 83 WITH 80 ppm CHLORINE	82
46	TRANSMITTANCE CURVES FOR ACID BLUE 83 WITH 160 ppm CHLORINE	83
47	TRANSMITTANCE CURVES FOR MORDANT BLUE 1 WITH 80 ppm CHLORINE	84
48	TRANSMITTANCE CURVES FOR MORDANT BLUE 1 WITH 160 ppm CHLORINE	85

FIGURES (Continued)

		PAGE
49	TRANSMITTANCE CURVES FOR DIRECT YELLOW 106 WITH 80 ppm CHLORINE	86
50	TRANSMITTANCE CURVES FOR DIRECT YELLOW 106 WITH 160 ppm CHLORINE	87
51	TRANSMITTANCE CURVES FOR DIRECT BLUE 86 WITH 80 ppm CHLORINE	88
52	TRANSMITTANCE CURVES FOR DIRECT BLUE 86 WITH 160 ppm CHLORINE	89
53	TRANSMITTANCE CURVES FOR DALTON SOLUTION NO. 1	90
54	TRANSMITTANCE CURVES FOR DALTON SOLUTION NO. 2	91
55	TRANSMITTANCE CURVES FOR DALTON SOLUTION NO. 3	92
56	TRANSMITTANCE CURVES FOR DALTON SOLUTION NO. 4	93
57	TRANSMITTANCE CURVES FOR ACID YELLOW 76 AT pH 4.0	94
58	TRANSMITTANCE CURVES FOR ACID YELLOW 76 AT pH 6.5	95
59	TRANSMITTANCE CURVES FOR ACID YELLOW 76 AT pH 8.5	96
60	TRANSMITTANCE CURVES FOR ACID ORANGE 86 AT pH 4.0 WITH 40 ppm CHLORINE	97
61	TRANSMITTANCE CURVES FOR ACID ORANGE 86 AT pH 6.7 WITH 40 ppm CHLORINE	98
62	TRANSMITTANCE CURVES FOR ACID ORANGE 86 AT pH 8.7 WITH 40 ppm CHLORINE	99
63	TRANSMITTANCE CURVES FOR ACID ORANGE 86 AT pH 4.0 WITH 80 ppm CHLORINE	100
64	TRANSMITTANCE CURVES FOR ACID ORANGE 86 AT pH 6.7 WITH 80 ppm CHLORINE	101
65	TRANSMITTANCE CURVES FOR ACID ORANGE 86 AT pH 8.7 WITH 80 ppm CHLORINE	102
66	CROSS SECTION OF IRRADIATOR	27

TABLES

No.		Page
1	Dyes Investigated	9
2	Chemical Oxygen Demand of Solutions Containing 0.25 g/ℓ of Dye	23

SECTION I

CONCLUSIONS

The following conclusions can be drawn from the experimental work done during the past year:

1. Solutions of commercial textile dyestuffs can be decolorized by a combined treatment using a chemical oxidant and gamma radiation.
2. The combined treatment is more effective than the effect of the two components applied separately.
3. Chlorine is a good oxidant for use in this process as it causes more decolorization and costs less than any other oxidant evaluated.
4. The combination treatment can be successfully used for the decolorization of mixtures of dyes, such as are used in commercial dyeing operations. There are no uniform decolorization effects that would make it feasible to predict the treatment effects for specific types of dyes.
5. The chemical oxygen demand of a dye solution is reduced by an amount approximately equivalent to the oxidizing potential of an added chemical oxidant; the reduction is slightly enhanced when radiation is also applied.
6. The biochemical oxygen demand of dye solutions is difficult to measure, but the values are low and are not appreciably altered by radiation treatment.
7. Some change in the total organic carbon content of dye solutions may be caused by treatment with chlorine with or without radiation.
8. Although some reduction in COD and possibly BOD occurs, the major benefit of the combined oxidation-radiation treatment of a dye waste would be the reduction of color.
9. A non-optimized preliminary estimate of treatment cost in a 240,000 GPD facility is $0.31 per thousand gallons for design treatment of 60 krads and 75 ppm chlorine.
10. Considerably less chlorine and radiation may be required in some cases depending on the particular effluent to be treated. Costs will be proportionately lower if less treatment is required.

SECTION II

RECOMMENDATIONS

This study has demonstrated the technical feasibility of treating textile dye wastes by the combined action of gamma radiation and chlorine. In order to establish the value of this process, it is recommended that:

1. A small pilot plant be constructed in order to provide data in a dynamic system for exploring more fully the potential utility of the process under conditions simulating industrial conditions.

2. Operating data from the pilot plant be used to estimate more precisely the cost of treatment for representative cases.

3. An optimized design for a large-scale operation be prepared. Various engineering configurations are possible and should be considered.

4. A commercial-size treatment facility utilizing this process be designed, and constructed if industrial support is forthcoming.

Preceding page blank

SECTION III

INTRODUCTION

Water pollution by waste effluents from textile mills presents an environmental problem in many regions of the country. Large volumes of waste water are generated,[1] and treatment is difficult because of the character of the waste.

Textile processing plants utilize a wide variety of dyes and other chemicals such as acids, bases, salts, wetting agents, retardants, accelerators, detergents, oxidizing agents, reducing agents, developers, stripping agents, and finishes. Most of these are not retained in the final textile product but are discarded after they have served their purpose. The liquid waste effluent of a textile plant may, therefore, contain any combination of such materials. As many textile processes are handled on a batch basis, concentrations of waste materials may fluctuate widely.[2]

Operational difficulties in a conventional waste treatment plant may be caused by the presence of compounds toxic to treatment plant biota or by fluctuations in the concentration of components of the waste. Poor results are obtained when materials resistant to biological attack are passed through biological treatment processes.[3]

Such inadequately treated effluents have very deleterious effects on receiving streams, and the situation is intensified when the stream flow is small, or industry is concentrated in a particular area.

Most of the dyes used by the textile industry are not readily degraded by ordinary treatment processes, and treated effluent may remain highly colored.[4] This very visible form of pollution is obvious to even the casual observer. Clearly, a need exists for an improved treatment process capable of destroying the color of textile wastes.

One possible process for the destruction of color due to organic compounds is treatment with ionizing radiation, possibly accompanied by a chemical oxidant.

It is well known that many organic molecules are strongly affected by ionizing radiation such as high energy gamma rays.[5] The effects may be intensified in aqueous solution where the products of radiolysis of water (free radicals, peroxides, and others) may also react with the organic

Preceding page blank

molecule. The presence of additional organic species or dissolved oxygen may alter the nature and the rate of the reaction involved. A dye such as methylene blue is decolorized in good yield when irradiated in aqueous solution in the presence of an excess of certain organic substances such as albumin, benzoate, ethanol, glucose, lactate, among others. Decolorization is inhibited by some materials such as thiourea and carbon dioxide. Yields are also dependent on the presence of dissolved oxygen, and at this stage it is not possible to predict a priori the result of irradiation of mixtures of compounds of the type under consideration.[6-11]

In waste treatment, organic molecules are usually degraded by oxidation through biological means, but chemical oxidation is also possible through use of chlorine, hydrogen peroxide, ozone, or other oxidants and could serve as a preliminary step in a combined treatment process.[12] Earlier work in this laboratory demonstrated the advantage of using both radiation and an oxidant.[13] Aqueous solutions of several commercial dyestuffs and also a textile dye waste of unknown composition were subjected to irradiation near a cesium-137 gamma ray source in both the presence and absence of chlorine. Without chlorine, complete decolorization, if it occurred, required a gamma dose of several megarads, necessitating a rather long exposure to the radiation source. In the presence of an excess of chlorine, color was destroyed during an irradiation time of a few minutes. With less chlorine present, color faded during irradiation but did not completely disappear for another 30-45 minutes. The combination of chlorine and radiation resulted in decolorization of all samples tested. These irradiation tests indicated that destruction of dye molecules may occur at exposures well below the sterilization dose, a factor of significance in assessing the potential cost of such treatment.

While efficiency of color removal was the prime consideration in evaluating this process, other factors had to be considered. Enhanced biodegradability of the treated solution is desirable, but more important is the possible production of a compound toxic to treatment plant biota. Evaluation of possible toxicity was therefore included in this project.

SECTION IV

EXPERIMENTAL DETAILS

Radiation Sources

Several irradiation facilities were employed in performing the test work and some work was done to develop additional equipment to enlarge the potential for performing dynamic flow tests.

1. Cesium-137 Source

A 12,000 curie cesium-137 source is available at Georgia Tech for static irradiation tests. This source is housed in a 20 ft deep, subsurface well and is arranged to provide uniform irradiation in an annular, coaxial configuration to as many as 12 vial specimens at a time. The dose rate in aqueous samples in the standard geometry is fixed at 1.0 Mrad per hour and total doses are varied by varying the exposure time. Sample insertion takes less than one second from a negligible field region.

2. Cobalt-60 Sources

To provide greater variability in total dose and dose rate and to obtain flow test capability, use was made of a number of high intensity cobalt-60 sources, ranging in activity from 5000 to 75,000 curies. These sources were available, through the courtesy of Gamma Industries, Inc., while they were stored in the storage pool at the Frank H. Neely Nuclear Research Center, at Georgia Tech, prior to secondary encapsulation. They were suspended in baskets about 15 ft below the pool surface and samples were irradiated in an aluminum pipe positioned an appropriate distance from the source. A dose calibration curve was obtained in this arrangement by means of thermoluminescent dosimeters.

3. Reactor Activation Source

Before the cobalt-60 sources became available for this work, consideration was given to the utilization of the Georgia Tech Research Reactor as a source of intense gamma radiation in a shielded facility outside the reactor itself. This activity would be produced by circulating a solution of a high-capture-cross section material, such as manganese or aluminum through a loop system inserted in one of the reactor beam holes.

The solution would be activated in passing through the flux region in the reactor; it would then flow through an external loop system where the dye samples could be irradiated statically or dynamically. By choosing a fairly short-lived target material, the activity would decay away rapidly whenever the reactor is shut down or the circulation loop is turned off, making access for tests or modifications simple and safe. A design study of such a system was performed as well as some computations on radiation fields and equilibrium activation levels. Some of these details will be found in Appendix B.

Procedure

In the initial phase of this work, aqueous solutions of commercial dyes were used. These were prepared at a concentration of 0.25 g/ℓ which was considered to be the maximum dye content of any normal textile waste effluent. This concentration proved to be very convenient as solutions were seldom completely decolorized, and it was therefore possible to determine relative resistance to treatment of the colored solutions.

It is to be noted that, in actual textile finishing practice, a waste containing a dye concentration this high would seldom be encountered.[14] The transfer of dye to fiber is usually efficient enough to leave a lower dye concentration in the dye bath itself. When diluted with other effluents, the actual dye concentration is therefore lower. In very concentrated test solutions, particularly those with dark color, treatment may actually destroy much of the color, but the change in transmittance is not easily observable because of the large concentration of dye molecules. If treated and untreated solutions are diluted and then compared, the difference in transmittance is readily apparent. The effects of treatment were more readily observed with lighter colored or less concentrated solutions without further dilution.

The actual dyes were chosen on the basis of their chemical composition, their manner of use, and the quantity being used. Selections were made after discussions with a large textile finisher and a major dye manufacturer.

Table 1 lists the various dyes used in the study. In addition to the trade name, the Colour Index[15] name and number are given where this information is available.

Table 1. Dyes Investigated

Trade Name	Colour Index Name and Number	
Artisil Blue Green 100%	Disperse Blue 7	62500
Artisil Violet RL	Disperse Violet 18	-
Azo Silk Red 3B 100%	Acid Red 151	26900
Benzyl Cyanine 6B	Acid Blue 83	42660
Benzyl Fast Yellow GNC	Acid Yellow 76	18850
Benzyl Fast Yellow 2CG	Acid Yellow 40	18950
Brilliant Alizarine Milling Violet FBL	Acid Violet 48	-
Calcocid Fast Yellow 36 Ex.	Acid Yellow 34	18890
Calcofast Neutral Red 3 GL	-	-
Calcofast Neutral Yellow R	Acid Yellow 152	-
Calcosperse Blue CG	Disperse Blue 73	-
Calcosperse Yellow 4RL	Disperse Yellow 23	26070
Denivat Blue 57	-	-
Kiton Fast Blue 4GL	Acid Blue 23	61125
Lanasyn Black M	Acid Black 107	-
Lanasyn Orange RL	Acid Orange 86	-
Lanasyn Yellow LNW	Acid Yellow 151	-
Latyl Cerise N	-	-
Latyl Cerise Y	-	-
Lumicrease Yellow EFUL	Direct Yellow 106	-
Merpacyl Red G	Acid Red 337	-
Neolan Blue 2G	Acid Blue 158	14880
Nylosan Blue E-2GL	Acid Blue 40	62125
Pyrazol Fast Turquoise GLL	Direct Blue 86	74180
Sandothrene Blue NGR	Vat Blue 6	69825
Sodyesul Brown GNCF	Sulfur Brown 14	53246
Acid Red 18	Acid Red 18	16255
Disperse Violet 4	Disperse Violet 4	61105
Mordant Blue 1	Mordant Blue 1	-

A number of actual dye wastes have also been studied. These solutions were obtained from textile finishing plants at Dalton and Columbus, Georgia and Lanett, Alabama. Most of the samples were taken directly from operating dye becks and consequently contain a higher concentration of dye than would have been present in the waste at the conclusion of the dyeing operation. The composition of these dye baths is a trade secret, but all of them are mixtures of different dyes, blended to produce a desired color. A typical dye bath may contain as few as two dyes or as many as seven or more, but the average seems to be about 3 or 4. Chemical additives such as wetting agents, dispersing agents, and dye assists, are also typically present.

The wavelength of minimum transmittance of each solution was determined by examination of the visible spectrum obtained with a recording spectrophotometer. Subsequent readings of transmittance of that solution were all made at the same wavelength. Experiments involving the effects of an oxidant without radiation were performed by adding the oxidant to the test solution, mixing, then transferring a sample to a spectrophotometer cuvette. The non-recording spectrophotometer was adjusted to the appropriate wavelength, and readings of transmittance were made at intervals as desired.

In experiments involving both radiation and an oxidant, the oxidant was added to 15 ml of the test solution which was in a 20-ml screw-cap culture tube. The tube was quickly capped, and the solution mixed by inverting the tube several times. The tube was then lowered into the opening of the radiation source, and timing was started as the tube entered the radiation field. After the desired period of irradiation, the culture tube was withdrawn from the radiation field, and a sample of the solution placed immediately in the spectrophotometer. The transfer of material from the radiation field to the spectrophotometer required only a few seconds, so readings could be easily taken as early as one minute after the end of the irradiation period.

Transmittance readings were usually continued at intervals as long as significant changes were being observed. In some cases this required an hour or longer, but more frequently the major changes had occurred in less than 10 minutes. Some experiments were performed in which the oxidant

was added while the test solution was in the radiation field. This was accomplished by placing the oxidant in a pipette to which a rubber tube and bulb were attached. The long narrow tip of the pipette was positioned near the bottom of the test solution so that pressure on the bulb caused the oxidant to be expelled into the test solution. The air expelled with the oxidant provided a thorough mixing of the oxidant with the test solution.

The initial experiments were all performed using the 12,000 curie cesium-137 source which provides a uniform radiation field of constant intensity. Later experiments utilized the cobalt-60 source with which control of the radiation intensity was possible.

Determination of biochemical oxygen demand and chemical oxygen demand was carried out according to the customary procedures which are described in Standard Methods.[16] Measurements of total organic carbon were made with a Beckman Total Organic Carbon Analyzer, Model 915, utilizing a Hamilton automatic syringe.

Solutions of dyes of a number of different chemical types have been subjected to treatment with radiation alone, a chemical oxidant alone, and with both radiation and an oxidant. Experiments with sodium hypochlorite, hydrogen peroxide, chlorine dioxide, and ozone revealed that the hypochlorite is the most effective, although estimation of ozone concentration was not very accurate. Sodium hypochlorite was used in most of the experimental work, although gaseous chlorine would probably be used in large-scale operations. The effect is the same, according to the following equations. Chlorine in dilute solution gives:

$$Cl_2 + H_2O \rightarrow 2H^+ + Cl^- + OCl^-$$

Sodium hypochlorite in dilute solution is essentially ionized:

$$NaOCl \rightarrow Na^+ + OCl^-$$

Sodium hypochlorite concentrations are hereafter expressed in terms of their chlorine content.

The various dyes studied will be discussed individually, although attention will be drawn to similarities and differences in behavior between different dyes. It is to be noted throughout this report that the

initial transmittance reading for a given dye is not always the same. These differences, usually no more than two or three percent, are caused by instability of the spectrophotometer and slight variations in the weighing and mixing of the solution. Ageing of solutions may also be accompanied by change in transmittance; fresh solutions were frequently prepared. Precise details of the radiation chemistry are difficult to establish owing to the proprietary nature of most of the dye formulations. In general terms, the dye degradation is probably determined by the rate of free ion generation in the water produced by irradiation and by the competing tendency for recombination of the individual dye molecules. The irradiation effects in ionizing and dissociating the dye molecules and the water molecules in most cases promote oxidation both by the chlorine present and by the oxygen ions in the radiolyzed water. An upper limit to this effect is set by backward reactions in the water and the finite mobility of the dye molecules and chlorine ions.

SECTION V

TEST RESULTS

Comparison of Oxidants

Acid Yellow 40, a monoazo type dye, and Disperse Violet 18, an anthraquinone, were used to compare the relative effects of sodium hypochlorite, chlorine dioxide, and hydrogen peroxide. The results are summarized in Fig. 1 and Fig. 2, where the time scale begins at the moment the reagent was added to the dye solution. It may be seen that hydrogen peroxide, either with or without radiation, is the least effective of the chemical reagents. Sodium hypochlorite with radiation is the most effective treatment for Acid Yellow 40, but chlorine dioxide plus radiation is the most effective by a slight margin for Disperse Violet 18. The slight advantage of chlorine dioxide is offset by its considerably higher cost, and subsequent work was confined to the use of sodium hypochlorite.

Treatment of Dye Solutions

To understand the results for the various dye solutions tested, it is important to point out certain common features that appear in the majority of the figures that follow. In comparing irradiated samples with those treated with chlorine only, optical transmittance is plotted against a common time scale. In general, decolorization occurs with chlorine treatment alone at a slow rate indicated by a nearly straight line in most cases. When a sample is irradiated, the first point shown is measured immediately after removal from the gamma source. Different exposures account for the different starting time for irradiated samples. From the time of removal, transmittance in general is seen to increase further, usually at a rate parallel to the "chlorine only" or "no gamma" line. The increase in transmittance due to the combined effect of radiation and chlorine is the effect desired in these tests. By extrapolating back the final slope of the transmittance curves one can obtain a measure of the beneficial effect of the combined treatment. In the cesium source with its fixed dose rate, the minimum gamma doses required for a given effect are not directly obtainable. This aspect will be discussed in a later section.

Anthraquinone Dyes

Acid Blue 23 (Kiton Fast Blue 4 GL) -- This dye responds readily to the combination radiation-oxidant treatment. Sodium hypochlorite at 80 ppm chlorine produces higher transmittance values than 40 ppm chlorine at each radiation dose, but 160 ppm produces effects almost identical to 80 ppm. The optimum treatment would seemingly consist of 80 ppm chlorine plus 35-50 krads. Graphs showing the results of different hypochlorite levels for different radiation doses in neutral solutions are shown in Figs. 3, 4, and 5.

Acid Blue 40 (Nylosan Blue) -- Decolorization of this dye is proportional to both the hypochlorite dose and the radiation dose. The best results were obtained from 160 ppm chlorine and 170 krads (94% transmittance), but the same chlorine dose with half as much radiation does nearly as well (88% transmittance). These results are graphically presented in Figs. 6 and 7.

Acid Violet 48 (Brilliant Alzarine Milling Violet FBL) -- Sodium hypochlorite alone is rather effective in the decolorization of this dye, but the effect is enhanced by radiation. At the 80 or 160 ppm chlorine concentration, high transmittances result upon standing. Irradiation enhances the effect by producing higher transmittances more rapidly. These findings are detailed in Figs. 8 and 9.

Disperse Blue 7 (Artisil Blue Green 100%) -- Treatment with 17 krads of gamma radiation with 160 ppm chlorine shows little improvement over the chlorine alone. A marked improvement results when the radiation dose is increased to 85 krads. See Fig. 10.

Disperse Violet 4 -- This dye is sparingly soluble in water, although it is well dispersed by chemical agents present in the commercial material. In order to achieve a true solution, the water dispersion was mixed with an equal volume of methanol or ethanol. Disperse Violet 4 is very soluble in these alcohols, and a true solution was obtained with either of them.

The methanol-water solution was treated as shown in Fig. 11, where it appears that sodium hypochlorite is more effective alone than in combination with radiation. The same behavior occurs in ethanol-water, with either 80 or 160 ppm chlorine, as illustrated in Figs. 12 and 13. These results are interpreted as indicating that, in the absence of radiation,

the hypochlorite reacts with both dye and alcohol. Reaction with the methanol is favored because more methanol is present; this leaves more unreacted dye.

Vat Blue 6 (Sandothrene Blue NGR) -- Comparisons were made of the behavior of this dye in water, water-methanol, and water-ethanol. In water, 80 ppm chlorine had no effect in the absence of radiation. Radiation doses of a few kilorads were ineffective, but a one megarad dose produced a distinct decrease in transmittance. When the dye was dissolved in water-methanol, 80 ppm chlorine was not very effective with or without radiation. Transmittances were somewhat improved by 80 ppm chlorine plus large doses of radiation. Details are set forth in Fig. 14.

Disperse Blue 73 (Calcosperse Blue CG) -- The behavior of this dye is typical of many of the dyes involved in this study. Figs. 15, 16, and 17 show the results of adding 40, 80, and 160 ppm chlorine, respectively. Fig. 15 shows that a minimum amount of chlorine is required for radiation to have a significant effect. Figs. 16 and 17 show that decolorization increases with increased radiation dose with an apparent leveling off at the higher doses. This is confirmed in Fig. 18 where the effect of radiation is shown on solutions containing different amounts of hypochlorite. It may be seen that the first 34 krad dose produces proportionally more effect than greater doses in the presence of 160 ppm chlorine. At 80 ppm chlorine, the radiation dose effect is linear up to 51 krads.

Latyl Cerise Y -- This material showed only low sensitivity to the radiation effect. At 40 ppm chlorine, added radiation increased the transmittance by a significant amount. At a hypochlorite content of 80 ppm chlorine, radiation effects were insignificant at a total lapsed time of 10 minutes. The transmittance continued to change rapidly after the end of the irradiation period; it appears that the continuing change is merely a manifestation of prolonged reaction with the hypochlorite. Figs. 19, 20, and 21 illustrate these results.

Azo Dyes

Acid Yellow 34 (Calcocid Fast Yellow 3G EX) -- In this dye, and the following, it was observed that chlorine alone led to rapid decolorization. Further or concomitant radiation exposure had little if any effect

as is seen in Fig. 22, bearing in mind that the initial slope in the longer irradiation is of no significance as such. The decrease in transmittance observed at 17 krad occurs in occasional samples; it may represent the formation of a light-absorbing species. However, since it is not evident in higher dose samples, it may be merely a transient condition.

Acid Yellow 40 (Benzyl Fast Yellow 2 CG) -- This dye is decolorized less readily than most of the compounds studied. One series of tests was made (see Fig. 23) and it was noted that at radiation doses less than 85 krads there was a slight recovery of color at 10 minutes after the start of the various radiation exposures. At a dose of 85 krads, no further change in transmittance was observed.

Acid Red 151 (Azo Silk Red) -- Two azo groups are present in the molecules of this dye, which is rather resistant to the various experimental conditions investigated. Sodium hypochlorite at the 80 ppm chlorine level has very little effect, about the same as 160 ppm chlorine. In both cases, the transmittance increase is proportional to the radiation dose, as shown in Figs. 24 and 25.

Acid Red 337 (Merpacyl Red G) -- This material decolorizes in an unusual nonlinear fashion in the presence of chlorine alone, as shown in Figs. 26 and 27. Adding irradiation to the process speeds up decolorization markedly and comparable decolorization is obtained in only a fraction of the time at 182 krad, compared with one hour in the presence of chlorine alone. Going to a megarad irradiation leads to the same ultimate decolorization as the one hour chlorination treatment, but it is evident that a saturation effect has occurred at much lower dosages.

Acid Blue 158 (Neolan Blue 2G) -- When treated with sodium hypochlorite at 40 ppm chlorine, this dye showed little response. When radiation was added, the response was greatly increased, as shown in Fig. 28. Higher transmittance values can be reached more rapidly with chlorine levels of 80 or 160 ppm, as illustrated in Figs. 29 and 30, respectively, for the usual dose values. It is interesting to note that the higher chlorine level leads to a significant reduction in the gamma-ray dose needed for comparable decolorization.

Disperse Yellow 23 (Calcosperse Yellow 4 RL) -- This water-insoluble disazo dye was dissolved in 50% methanol and was found to behave similarly to Disperse Violet 4 (Fig. 11). With no radiation applied, the

hypochlorite alone increases transmittance from 15.5 to 30% whereas 85 krad with no chemical oxidant produced almost no change. This is depicted in Fig. 31.

Metallized Azo Dyes

Acid Yellow 151 (Lanasyn Yellow LNW) -- Of intermediate resistance to decolorization, this dye responded to sodium hypochlorite at the 80 ppm chlorine concentration, but to a slightly greater extent and more rapidly when radiation treatment followed addition of the hypochlorite. See Fig. 32.

Acid Yellow 152 (Calcofast Neutral Yellow R) -- Sodium hypochlorite alone was quite effective in decolorizing this light-colored dye. Radiation at the 17 krad level did not increase the effect of the hypochlorite, although a dose of 170 krads caused a significant increase in transmittance. See Fig. 33.

Acid Orange 86 (Lanasyn Orange RL) -- Without radiation, sodium hypochlorite had little effect on this dye, as shown in Fig. 34. By treating also with 51-85 krads, very good decolorization was achieved.

Acid Black 107 (Lanasyn Black M) -- This product is the most resistant of the several metallized azo materials investigated. Sodium hypochlorite at 80 ppm chlorine produced a transmittance increase of about 6%, and even with the addition of 204 krads of radiation, the increase was only about 15% as shown in Fig. 35. The situation is improved, however, when the oxidant content is increased to 160 ppm chlorine and the radiation level is in the 85-170 krad dose range. Fig. 36 shows the results of this experiment.

Calcofast Neutral Red 3 GL -- Irradiation was necessary to produce any appreciable change in the color of this dye solution. As Fig. 37 reveals, the effect of hypochlorite alone is negligible, but 85 krads raised the transmittance from 7.5 to 31.5%, and 170 krads raised it to 82%.

Sulfur Dyes

Sulfur Brown 14 (Sodyesul Brown GNCF) -- It was found that decolorization of this dye could best be achieved with a sodium hypochlorite concentration of 160 ppm chlorine. The transmittance of the solution increased as the radiation dose was raised. This is similar to the results obtained with the other sulfur dye studied, Denivat Blue 57. The manner

in which these dyes are applied makes it unlikely that an effluent would ever contain a dye concentration as high as that of the test solutions. The experiments with Sulfur Brown 14 are summarized in Fig. 38 and a comparison of the relation between radiation dose and transmittance for both Sulfur Brown 14 and Denivat Blue 57 is shown in Fig. 39, compared 10 minutes from the start of the test in all cases. It is evident that Denivat Blue 57 is much more radiation-sensitive.

Denivat Blue 57 -- At 0.25 g/ℓ this sulfur dye of indeterminate structure shows little response to treatment with radiation and a sodium hypochlorite concentration of 40 ppm chlorine (Fig. 40). The 17 krad dose actually appears somewhat more effective than higher radiation doses, but the differences are small and none are very effective. Considerable improvement can be seen in Fig. 41 which illustrates the effectiveness of doubling the chlorine concentration to 80 ppm. The increase in transmittance with even the minimum radiation dose is significant. The best results were obtained when the chlorine content was 160 ppm (Fig. 42). After a 66 krad dose, the solution approaches 90% transmittance and appears almost clear upon visual inspection; it should be acceptable for any industrial effluent. The maximum applied dose of 83 krads raised the transmittance above 95%, and the solution appeared colorless to the eye.

When either 80 or 160 ppm chlorine are present, the transmittance increases proportionally with the radiation dose. This is shown in Fig. 43, where transmittance at six minutes after the beginning of the irradiation period is plotted against radiation dose, and in Fig. 39, for a different chlorine content.

Triphenylmethane Dyes

Acid Blue 83 (Benzyl Cyanine 6B) -- This material is one of the two triphenylmethane compounds studied. In aqueous solution it is decolorized appreciably by sodium hypochlorite alone at 40, 80, and 160 chlorine, but when radiation is applied, decolorization is more rapid and more complete. These results are shown in Figs. 44, 45, and 46. However, increasing either chlorine content or radiation dose leads to only marginal increases in final transmittance.

Mordant Blue 1 -- When sodium hypochlorite was added to a solution of this dye, almost no change in transmittance occurred. Transmittance is

greatly increased when radiation treatment follows addition of hypochlorite at a concentration of 80-160 ppm chlorine. The higher chlorine content gives a higher transmittance at 85 krads, but 80 ppm is equally as effective as 160 ppm when the radiation dose is 170 krads. These conclusions are drawn from Figs. 47 and 48.

Dyes of Other Chemical Types

Direct Yellow 106 (Lumicrease Yellow EFUL) -- The exact chemical formula of this dye is not published in the Colour Index, but it is listed as a stilbene type. It is the only dye of this type that was included in the study. By reference to Figs. 49 and 50, it is seen that the effect of sodium hypochlorite alone is negligible. Seventeen krads plus 80 ppm chlorine increases transmittance to 47% from an original of 12%, and if the radiation dose is held at 17 krads, 160 ppm chlorine raises the transmittance to 52%. Greater radiation doses are proportionally less effective. Optimum conditions for decolorization of this dye therefore appear to consist of approximately 17 krads of gamma radiation and chlorine in the range of 80 to 160 ppm. With this dye, no change in transmittance occurred following the irradiation period; all changes occurred during irradiation, since the chlorine effect alone was insignificant.

Direct Blue 86 (Pyrazol Fast Turquoise GLL) -- This is the only phthalocyanine type dye investigated during this study, and it is decolorized quite readily by a combined radiation plus hypochlorite treatment. The optimum combination appears to be in the range of 160 ppm chlorine and 68 krads of gamma radiation. Figs. 51 and 52 summarize the experimental work on this material. With this dye, there appeared to be slow-acting chlorine effects after irradiation that were different from those for chlorine acting alone.

Commercial Dye Wastes

To evaluate the usefulness of the combined oxidation-radiation treatment on actual dye wastes, samples were obtained from several textile mills. Solutions were collected directly from dye baths that were being used to dye fabric or yarn. None of the baths was exhausted, and the dye content was higher than it would have been at the completion of the dyeing process. Also, the usual dilution with other plant effluent had not occurred, so these solutions were several times more concentrated

than the flow normally released by the plant.

As the composition of these solutions is unknown, they were numbered for identification purposes. The liquid labeled Dalton No. 1 was reddish-brown in color, and responded to treatment with sodium hypochlorite at 80 ppm chlorine. When treated additionally with 51 krads of radiation, the solution exhibited a transmittance increase from 10 to more than 55%. This information is detailed in Fig. 53.

Dalton solution No. 2 was a very pale straw color, and would have presented no objectionable color had it been discharged directly to a stream. At the wavelength of maximum absorbance, it transmitted 81%, and this value was increased by 6% when 40 ppm chlorine was added. When subjected to irradiation, transmittance values remained constant or declined slightly as revealed in Fig. 54. The behavior and appearance of this solution make it seem doubtful that the color is due solely to an organic dye; other processing chemicals may be the source of color.

Dalton solution No. 3 was a deep yellowish-brown; it was diluted with an equal volume of water before treatment. It did not respond very well until the sodium hypochlorite level was raised to 160 ppm chlorine. At this chlorine concentration, decolorization was proportional to the radiation dose, as shown by Fig. 55.

Dalton solution No. 4 was a very opaque dark green that had been in use for only a few minutes, so its concentration was near the maximum. It was necessary to dilute it with 3 volumes of water in order to obtain a transmittance of as much as 5%. Sodium hypochlorite alone at 160 ppm chlorine produced little effect, but when radiation was included, transmittance values around 70% were obtained as illustrated in Fig. 56.

Effect of pH on Decolorization of Dye Solutions

A series of experiments was performed in which phosphate buffers were used to obtain pH values in the ranges of 4.0, 6.5, and 8.7 in the dye solutions. No broad generalizations are possible with the small number of dyes investigated, as no distinct relationship was found between ease of decolorization and pH. In some instances the lowest pH produced the greatest effect, and in other instances the least effect. The effects on some dyes were the same at all three pH values.

Acid Yellow 76 (Benzyl Fast Yellow GNC) -- This dye was tested at three pH values in the presence of sodium hypochlorite at the 40 ppm chlorine level. Radiation was supplied by cobalt-60 at 8000 rads/minute. A dose of 40 krads raised the transmittance from its initial 17.5% to the 55-60% range at all pH values; transmittance then declined to 40% at pH 4.0 and 6.5, while the decline was only to about 48% at pH 8.5. With 8 or 24 krad doses the first post-irradiation readings were all in the 65-75% range, but subsequent readings all declined with the single exception of the sample which received 8 krads at pH 4.0. Figs. 57, 58, and 59 illustrate these findings. No pH readings were obtained during the tests and the pH may well be changed by the irradiation.

This effect will require further investigation, especially under flow conditions.

Acid Orange 86 (Lanasyn Orange RL) -- This dye exhibited no color recovery under any conditions utilized. When a solution of this dye was subjected to radiation from cobalt-60 at 6000 rads/minute, the transmittance was increased most at pH 4.0 for any radiation dose. A somewhat lesser effect was noted at pH 6.7 and the minimum effect at pH 8.7. These findings are set forth in Figs. 60, 61, and 62. Further experiments were performed with this dye in the presence of high hypochlorite concentrations. The general pattern of the curves at pH 8.7 (Fig. 63) is similar to those at pH 6.7 (Fig. 64), but differs markedly from the pattern at pH 4.0 (Fig. 65). The increased speed of decolorization at pH 4.0 is well illustrated by comparison of the readings at 20 minutes of the solutions receiving 6 krads. At pH 8.7 the transmittance is 21%; at 6.7, 24%; but at 4.0 it is 62%. All these effects are dominated by the extremely slow action of the chlorine on this dye. Note the longer time scale in these figures which are numbered 66 and 67. The effects of pH on the decolorization of several dye solutions by sodium hypochlorite plus radiation are discussed in detail in the Interim Report of August 31, 1971.[17] Information is given there on Acid Yellow 40, Acid Blue 23, Acid Red 18, and Acid Blue 158.

Biochemical Oxygen Demand of Dye Solutions

Determination of the biochemical oxygen demand (BOD) of dye solutions is difficult because of the low biodegradability of the dyes. BOD values

obtained using activated sludge as the seed were not satisfactory, so attempts at acclimatization were made. A portion of the activated sludge was placed in some of the dye solution and allowed to stand. In some instances the dye color faded, indicating that biological decomposition was occurring. The faded supernatant was replaced at intervals with fresh dye solution. After three or more days, some of the sludge was used to inoculate the dilution water used in the BOD test on the dye to which the sludge had presumably become acclimated. This required the preparation of a different seed for each different dye.

The results of the tests were disappointing. The values obtained were not very consistent and for the most part appeared independent of the amount of dye used in the determination. It was concluded that the dye itself was taking little, if any, part in the consumption of dissolved oxygen; the values obtained were due almost exclusively to nitrification. Ammonium ion is a component of the buffer used in preparing dilution water and is apparently utilized by the bacteria present. The results obtained with dye solutions subjected to radiation were indistinguishable from those obtained with untreated solutions.

Tests were made on Pyrazol Fast Turquoise GLL, Latyl Cerise Y, Sodyesul Brown GNCF, Acid Red 18, Acid Blue 158, Acid Blue 23, and Acid Yellow 40. It is concluded from these determinations that the BOD exerted by these dyes is very small and perhaps zero, and a few kilorads of radiation dose has little or no effect on the BOD.

Chemical Oxygen Demand of Dye Solutions

The chemical oxygen demand (COD) test indicates the quantity of material present in water or a waste that is chemically oxidizable under specified conditions. Although some inorganic interference is possible, it is taken as a measure of organic matter present. There is a rough correlation between COD, biochemical oxygen demand (BOD), and total organic carbon (TOC) in some instances, but large differences may exist. COD determinations are very useful as they can be made in a few hours while a standard BOD requires a five day incubation period. COD is also used to determine organic loads when the presence of toxic substances precludes measurement of BOD.

The results of a number of COD determinations are summarized in Table 2.

Table 2. Chemical Oxygen Demand of Solutions Containing 0.25 g/ℓ of Dye

Trade Name	Colour Index Name	Untreated Solution	80 ppm Chlorine	80 ppm Cl_2 + 85 krads
Acid Red 18	Acid Red 18	245*	171*	167*
Artisil Blue Green 100%	Disperse Blue 7	317	---	---
Azo Rhodine 6B	Acid Violet 7	91	---	---
Benzyl Fast Yellow 2CG	Acid Yellow 76	191	134	132
Brilliant Alizarine Milling Violet FBL	Acid Violet 48	163	---	---
Calcocid Fast Yellow 3G EX	Acid Yellow 34	278	193	193
Calcofast Neutral Blue 3GL	Acid Blue 171	307	234	230
Calcofast Neutral Red 3GL	----	152	---	---
Calcofast Neutral Yellow R	Acid Yellow 152	275	---	---
Calcospere Blue CG	Disperse Blue 73	355	284	280
Calcospere Red FFB	Disperse Red 60	294	---	234
Calcosyn Brilliant Scarlet BN	Disperse Red 1	370	297	282
Calcosyn Sapphirine Blue 2GS	Disperse Blue 3	317	234	232
Calcosyn Yellow GCN	Disperse Yellow 3	373	---	303
Cibalan Navy Blue RL	----	270	200	192
Kiton Fast Blue 4 GL	Acid Blue 23	93	54	57
Lanasyn Black M	Acid Black 107	124	---	---
Lanasyn Yellow LNW	Acid Yellow 151	280	---	---
Latyl Cerise Y	----	303	229	217
Lumicrease Yellow EFUL	Direct Yellow 106	89	---	---
Mordant Blue 1	Mordant Blue 1	128	80	80
Neolan Blue 2G	Acid Blue 158	110	63	63
Nylosan Blue E-2GL	Acid Blue 40	280	---	---
Waste dye effluent	----	257	238	229

*All values are expressed in µg/1.

It is to be noted that there is wide variation in the COD of the untreated solutions although they were all prepared at the same concentration, 0.25 g/ℓ. These differences are due to some degree to differences in the chemical structure of the dye molecules, but primarily to differences in the organic content of the commercial dyestuff. The actual compound which produces color may be blended with dispersants, wetting agents, or other non-colorants; the commercial product may also contain an inert diluent to provide the proper concentration for commercial application.

The general pattern observed was that the initial COD of the solution was reduced more by combined oxidation-radiation treatment than by oxidation alone, although the differences were small. The amount of change is proportional to the susceptibility of the dye to oxidation by the sodium hypochlorite with or without radiation. Radiation alone in small doses has been shown to produce little change in color, and it is reasonable to expect only limited accompanying changes in the COD value at the radiation levels used in this work. To obtain significant changes in COD values in dye solutions, doses in the megarad range would need to be employed, as shown by Garrison et al.[18]

Effect of Radiation Dose Rate

If it is assumed that the combined radiation-chlorine effect is due to the competition between chlorine and radiolysis products in the solution bath for interaction with dye molecules on the one hand and backward recombination reactions on the other, then the decolorization process should depend primarily on the total dose received, since the chlorine-induced oxidation process is relatively slow. Some dose-rate dependence may be expected where total decolorization effects are large and rapid.

A few tests have been conducted in the cobalt facility to test for optimum dose and dose-rate dependence. Since this information is crucial for the optimization of the treatment facility design, further tests will need to be conducted for several of the more important sample solutions.

Acid Blue 23 was irradiated for various lengths of time at dose rates of 6000 rads per minute and 13,000 rads per minute, with a constant amount of added sodium hypochlorite. At a pH of 8.7, there was no great difference between effects produced by different dose rates if the total dose was similar and transmittance was measured at about 45 minutes or later.

Higher transmittance values were generally associated with higher doses, as shown in Figs. 66 and 67, although the 13 krad dose gave a transmittance value lower than at 6 krads. Figs. 68 and 69 show that the situation is different at pH 6.4 where a 39 krad dose at 13 krad/minute gave the same results as 60 krad at 6 krad/minute. Figs. 70 and 71 show a less distinct pattern at pH 4.6. The highest dose, 65 krad, was least effective, and 39 krad was found to be most effective. The recovery shown on the 65 krad curve may be due to recombination, producing compounds with lower transmittance values.

From consideration of these findings it is concluded tentatively that radiation delivered at the rate of 13,000 rads per minute is more efficient than radiation supplied at 6000 rads per minute. However, this dose rate is not necessarily the optimum for this compound, let alone for any combinations of dyes.

Preliminary Cost Evaluation

In order to make a rough estimate of the costs involved in applying the oxidation-radiation treatment to wastes on a plant-size scale, it was necessary to assume certain design factors. Two alternates are possible in positioning this process in the treatment sequence. It could be used as the final step in a municipal or combined treatment plant before releasing the effluent to the receiving stream. Many effluents are chlorinated at least to some degree just prior to release, and at this stage the cost of chlorine would be minimized. The obvious disadvantage of this situation is the high volume of waste that would have to be treated. The highly colored dye wastes usually constitute only a fraction of the textile waste produced, and this would be diluted much more by other non-colored industrial or domestic sewage.

The alternative is to treat colored wastes at their point of maximum concentration before they receive any dilution. This appears to be a more likely arrangement, as the lower volume of liquid would allow smaller physical facilities, and the effects of the oxidant and radiation would be concentrated on the dye itself and not dissipated on other matter present at later stages of treatment. The following design and cost considerations are therefore based on having this process as the initial step in the treatment scheme.

Functionally, the facility would consist of chlorine injection, mixing of chlorine with the waste flow, and retention of the mixture in a radiation field for the time required to absorb the necessary radiation dose. The addition of chlorine to a liquid flow is a very common procedure, and can be accomplished very readily with an injector inserted into the pipe carrying the waste. Mixing can be accomplished by turbulence in the pipes which can be easily created with vanes or baffles. The irradiator itself is visualized as a pipe or channel, about 3 feet in diameter. The cobalt-60 which provides gamma radiation would be contained in tubes a few inches in cross section positioned inside the large pipe. Optimization studies have not been made to determine the most efficient configuration, but a symmetrical arrangement of four of the small tubes is assumed for purposes of calculation. The large channel will be considered 100 ft in length for purposes of calculation, and the isotope-containing tubes will total 400 ft. Encapsulation will be in one foot lengths, so a total of 400 elements will be needed. The channel need not be in a straight line and could consist of several folded segments.

The treatment characteristics chosen were 75 ppm chlorine and 60 krads of radiation. Actual operating conditions will be determined by the chlorine feed rate and the flow rate of the waste through the irradiator. As both of these factors can be easily controlled, a very flexible arrangement will be provided.

The actual capacity of the facility depends on the flow rate chosen; twice the amount of waste could be treated if the required radiation dose were halved. Excess chlorine injection capacity would be provided by selecting an injector larger than required for the design flow. Chlorine addition would therefore not be the limiting factor.

A waste flow of 10,000 gallons per hour was assumed, and the design radiation dose of 60 krads is to be delivered in ten minutes; this requires an irradiation volume of 227 cubic feet.

The dose calculation is as follows:

A dose of 60 krads/10 min is desired, and

60 krads/10 min = 360 krad/hr

$$\frac{(3.6 \times 10^5 \text{ rads/hr})(1 \text{ g/cm}^3)(2.83 \times 10^4 \text{ cm}^3/\text{ft}^3)(2.27 \times 10^2 \text{ ft}^3)}{(3.6 \times 10^3 \text{ sec/hr})(2.5 \frac{\text{MeV}}{\text{dis}})(1.6 \times 10^{-6} \text{ ergs/MeV})(1 \times 10^{-2} \frac{\text{rads}}{\text{ergs/g}})}$$

$$= \frac{23.13 \times 10^{11}}{14.40 \times 10^{-5}} = 1.61 \times 10^{16} \text{ dis/sec}$$

$$\frac{1.61 \times 10^{16} \text{ dis/sec}}{3.7 \times 10^{16} \frac{\text{dis/sec}}{\text{MCi}}} = 0.43 \text{ MCi}$$

Therefore, 0.43 MCi is the amount of Co-60 needed to treat a volume of 227 ft^3 to a dose rate of 60 krads/10 min. This calculation assumes 100% source utilization and that all parts of the waste flow receive this minimum dose rate while passing through the radiation zone.

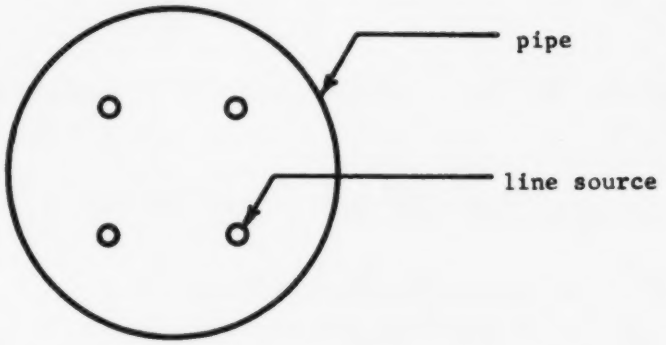

Figure 66 Cross Section of Irradiator

The irradiator contains within it four line sources each of which is 100 feet long. A cross section of the proposed configuration is shown in the figure above.

In order to maintain a minimum cobalt-60 inventory of 0.43 MCi, it is necessary to start with a larger amount. Since Co-60 decays about 12% per year: $0.43 + .125\ (0.43) = 0.484$ MCI

initial cost = $(4.84 \times 10^5$ Ci)($0.1/Ci) + $75/element (400 element)

$= 4.84 \times 10^4 + 3 \times 10^4 = 7.84 \times 10^4$ $ for Co-60

Irradiator and installation costs = 1×10^4 \$

This cost will be amortized over a 20 year period, semi-annually, at 6% interest per year.

From an annuity rent table[19] the cost is obtained:

0.08654 dollar/dollar/year

or

\$7,649/yr including interest

The cost to replace 12.5% of the Co-60 each year is

$(\$7.84 \times 10^4)(0.125/yr) = \$9,800/yr$

The salvage value of Co-60 remaining at the end of 20 years is estimated at half its initial cost, which gives a per year credit of

$$\frac{\$43,000}{2 \times 20} = \$1,075$$

The total cost per year with the semi-annual payment plan is:

Principle and interest	7,649
Annual isotope replacement	9,800
Salvage value	1,075
	\$16,374

At the design flow rate and a radiation dose of 60 krads, the cost of radiation is

$$\frac{1.6 \times 10^4 \ \$/yr}{0.876 \times 10^8 \ gal./yr} = \$0.183/1000 \ gal.$$

The cost of chlorine waa calculated as follows:

Amount required per thousand gallons at 75 ppm:

1000 gal. x 8.337 lbs/gal. = 8337

8337 x .000075 = 0.625 lb

Half the chlorine injected will form hypochlorite in the reaction with water, so twice as much or 1.25 lbs. At the current chlorine price of \$0.10/lb, the cost is

\$0.10/lb x 1.25 lbs/1000 gal. = \$0.125/1000 gal.

The total cost is therefore

$\$0.183 + \$0.125 = \$0.308 \cong \$0.31/1000$ gal.

The amount of radiation and chlorine required will depend on the concentration and composition of the waste being treated. Based on the experiments performed, it appears that all normal effluents could be adequately treated at the design levels of 60 krads and 75 ppm chlorine. Where dye concentration in the waste is at a lower level or the color-producing material is particularly sensitive to treatment, much higher volumes of waste can be treated at proportionately lower unit costs.

SECTION VI

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the advice and assistance received from many sources during the performance of this project. Mr. Charles Ris, Office of Research and Monitoring, Environmental Protection Agency, Washington was project manager and Mr. Edmond P. Lomasney of the Southeastern Office of the EPA was project officer. Their assistance and cooperation has been outstanding.

The project was carried out under the supervision of project director Dr. T. F. Craft, Senior Research Chemist and grant director, Dr. G. G. Eichholz, Professor of Nuclear Engineering. Others who were significantly involved in the work were graduate research assistants Luis Y. Garcia, R. D. Morris, Iqbal K. Mozawalla, Harry T. Taylor, and James T. West. Mr. S. N. Millspaugh, research assistant, deserves particular mention because of his careful preparation of the numerous graphs.

Thanks are due to those who furnished samples of dyes and dye solutions. The A. French Textile School supplied several commercial products and also some purified materials. We are particularly indebted to Mr. Lewis M. Redd of the Atlanta Office of Sandoz, Inc. He not only sent numerous dye samples, but was a continuing source of needed information. Other manufacturers who cooperated were Southern Dyestuff Company and American Cyanamid Company, both of Charlotte, N. C.

Mr. V. D. Parrott, Director of Utilities, City of Dalton, Georgia was most helpful with information and discussions on the general and specific aspects of textile waste disposal problems. He also introduced Mr. W. K. Newman of West Point-Pepperell, Cabin Crafts Division, who showed us the operation of a large dyeing operation and furnished numerous samples of dye bath solutions.

We acknowledge and thank Gamma Industries, Inc. for allowing us to use some of their cobalt-60 as a gamma source while it was being processed at the Frank H. Neely Nuclear Research Center of the Engineering Experiment Station.

Preceding page blank

The keen interest of personnel of the Georgia State Water Quality Control Board is appreciated. These include Mr. Warren O. Griffin, assistant to the executive secretary, Mr. Charles H. Starling, retired director of industrial waste services, and his successor, Mr. William M. Jernigan.

SECTION VII

REFERENCES

1. Hyden, W. L., Becknell, D. F., and Elders, T. E., "Survey of the Nature and Magnitude of the Water Research Needs of the Textile Industry of Georgia," Water Resources Center, Georgia Institute of Technology, Report WRC-0366 (1966)

2. Arnold, L. G., "Forecasting Quantity of Dyestuffs and Auxiliary Chemicals Discharged into Georgia Streams by the Textile Industry," M.S. Thesis, Georgia Institute of Technology, Atlanta, Georgia (1967)

3. Besselievre, E. B., "The Treatment of Industrial Wastes," McGraw-Hill Book Company, New York (1969)

4. Flege, R. K. "Determination of Degraded Dyes and Auxiliary Chemicals in Effluents from Textile Dyeing Processes," Environmental Resources Center, Georgia Institute of Technology, Report ERC-0270 (1970)

5. Swallow, A. J., "Radiation Chemistry of Organic Compounds," Pergamon Press, New York (1960)

6. Crapper, W. H., "The Radiation Chemistry of Organic Dyes," Sandia Corporation, SCTM 139-59 (16), 1959

7. Hayon, E., Scholes, G., and Weiss, J., "Chemical Action of Ionizing Radiations in Solution. XIX. Some Aspects of the Reduction of Methylene Blue by X-rays in Aqueous Systems," J. Chem. Soc. 301-311 (1957)

8. Day, M. J., and Stein, G., "Chemical Effects of Ionizing Radiation in Some Gels," Nature 166, 146-7 (1950)

9. Stein, G., "Some Aspects of the Radiation Chemistry of Organic Solutes," Disc. Faraday Soc. 12, 227-234 (1952)

10. Dale, W. M., "Protection Effect and Its Specificity in Irradiated Aqueous Solutions," Disc. Faraday Soc. 12, 293-99 (1952)

11. Minder, W., and Heydrich, H., "Radiation Chemistry of Organic Solutions," Disc. Faraday Soc. 12, 305-312 (1952)

12. Fair, G. M., and Geyer, J. C., "Water Supply and Waste Water Disposal," John Wiley, New York (1954)

13. Craft, T. F., and Eichholz, G. G., "Synergistic Treatment of Textile Dye Wastes by Irradiation and Oxidation," Int. J. App. Rad. & Isotopes 22, 543-7 (1971)

14. Trotman, E. R., "Dyeing and Chemical Technology of Textile Fibres," third edition, Griffin, London (1964)

15. "Colour Index," 2nd edition, The Society of Dyers and Colourists, Yorkshire, England (1956)

16. "Standard Methods for the Examination of Water and Wastewater," Thirteenth edition, American Public Health Assn., New York (1971)

17. R. D. Morris, "Detection of Dye Degradation Products from Gamma Irradiation Processes Coupled with Oxydizing Reactions," M.S. Thesis, Georgia Institute of Technology, Atlanta, Georgia, August 1971

18. Garrison, A. W., Case, F. N., Smiley, D. E., and Kau, D. L., "The Effect of High Pressure Radiolysis on Textile Wastes, Including Dyes and Dieldrin," 5th International Conference on Water Pollution Research, San Francisco, July, 1970; Isotopes & Rad. Technol., 9, 101-104 (1971)

19. Minrath, W. R., "Handbook of Business Mathematics," D. Van Nostrand, Princeton, N. J. (1959), pg. 339

Additional references not directly quoted are the following.

Condren, A. J., "Radiation Induced Oxidation of Selected Organics in Waste Water," Ph.D. Thesis, Purdue University (1969)

Friedlander, G., Kennedy, J. W., and Miller, J., "Nuclear and Radiochemistry," 2nd edition, John Wiley, New York (1964)

Whittemore, W. L., et al., "Ionizing Radiation for the Treatment of Municipal Waste Waters," Gulf General Atomic Final Report GA-9924, Contract AT-(04-3)-167, A.E.C., Division of Technical Information (1970)

Lenz, B. L., et al., "The Effect of Gamma Irradiation on Kraft and Neutral Sulphite Pulp and Paper Mill Aqueous Effluents," Pulp and Paper Magazine of Canada 72, No. 2, T75-T80 (1971)

Ten papers on process radiation development appeared in Isotopes and Radiation Technology 8, No. 4, Summer, 1971. All of these are of interest in the water or waste-water field, but particularly pertinent are these:

Ballantine, D. S., "Potential role of radiation in waste-water treatment," page 415

Gerrard, Martha, "Sewage and waste-water processing with isotopic radiation-survey of the literature," page 429

Mytelka, A. I., "Radiation treatment of industrial waste waters: an economic analysis," page 444

Compton, D. M. J., "Destruction of organic substances in waste water by ionizing radiation," page 453

Ingols, R. S., "Factors Causing Pollution of Rivers by Wastes from the Textile Industry," Am. Dyestuff Reporter _, 358-359 (1962)

Prokert, K., and Stolz, W., "Dosimetry of Ionizing Radiations by Means of Solid Dye Systems," Isotopenpraxis 6, 325-330 (1970)

Michelsen, D. L., and Fansler, T. B., "The Treatment of Disperse Textile Dye Wastes by Fram Fractionation," Bull. 34, Water Resources Research Center, Va. Polytechnic Institute, Blacksburg, Va. (1970)

Publications

The portion of this work carried out by Mr. R. D. Morris was utilized as the experimental phase of a thesis in partial fulfillment of the requirements for a Master of Science degree in the A. French Textile School, Georgia Institute of Technology. This thesis was subsequently issued as an interim project report.

Morris, R. D., "Detection of Dye Degradation Products from Gamma Irradiation Processes Coupled with Oxidizing Reactions," M.S. Thesis, Georgia Institute of Technology (1971)

Morris, R. D., "Detection of Dye Degradation Products from Gamma Irradiation Processes Coupled with Oxidizing Reactions," Interim Report, FWQA Grant No. 12090 FZB, Georgia Tech Project B-391. Engineering Experiment Station, Georgia Institute of Technology (1971)

SECTION VIII

APPENDIX

A. GRAPHICAL PRESENTATION OF DATA

Preceding page blank

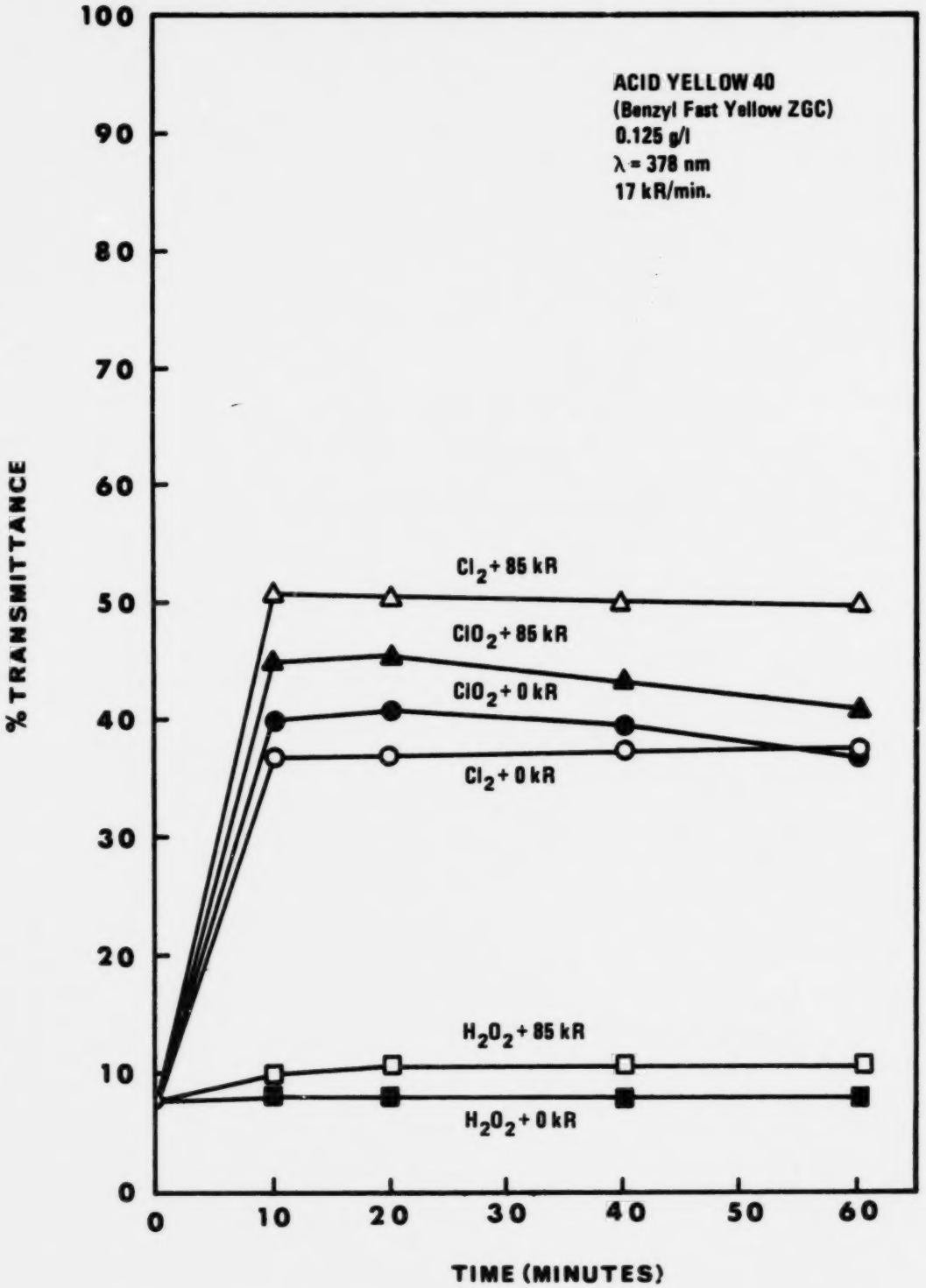

Figure 1 Transmittance Curves for Acid Yellow 40 at 0.125 g/ℓ

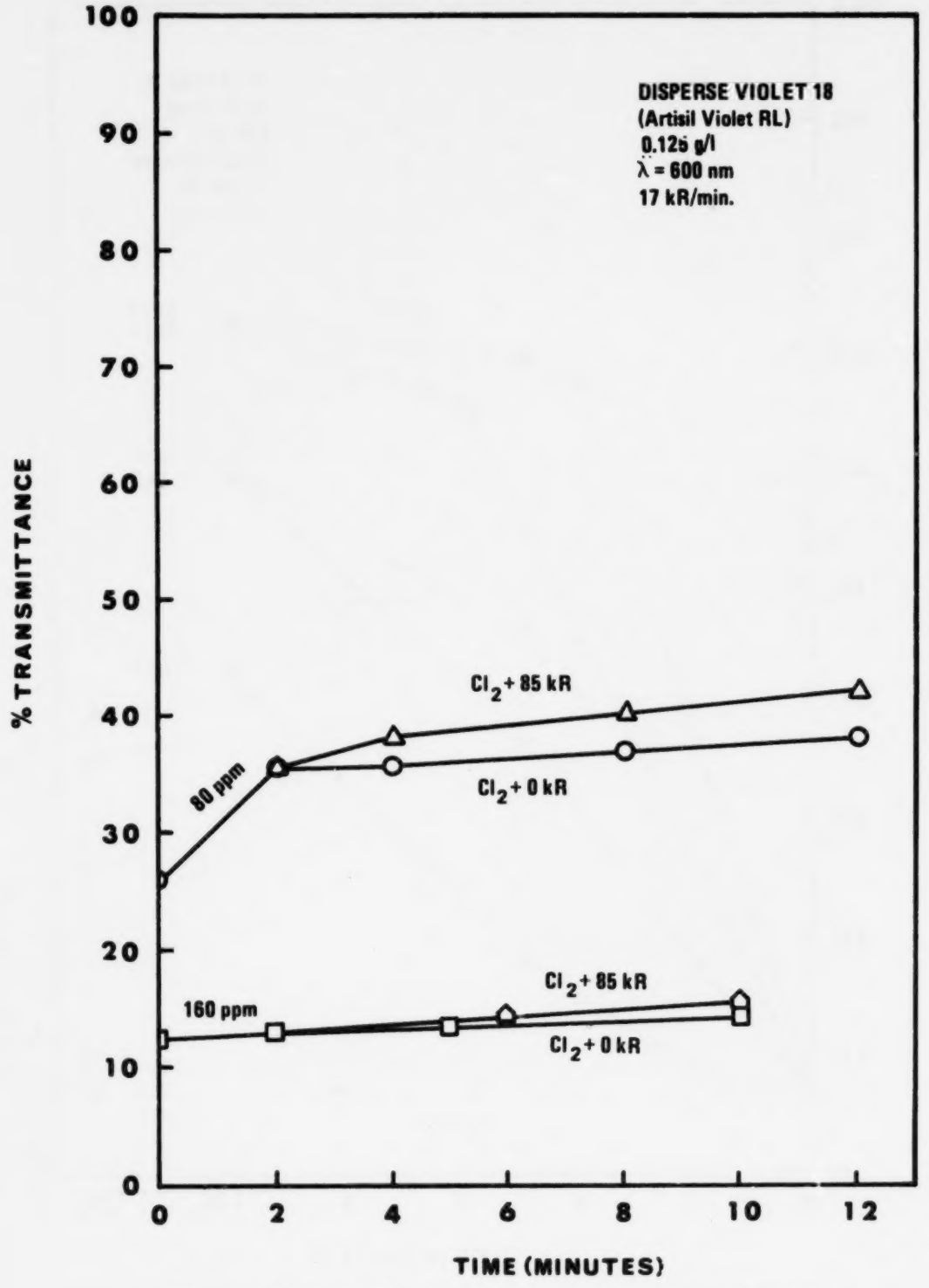

Figure 2 Transmittance Curves for Disperse Violet 18

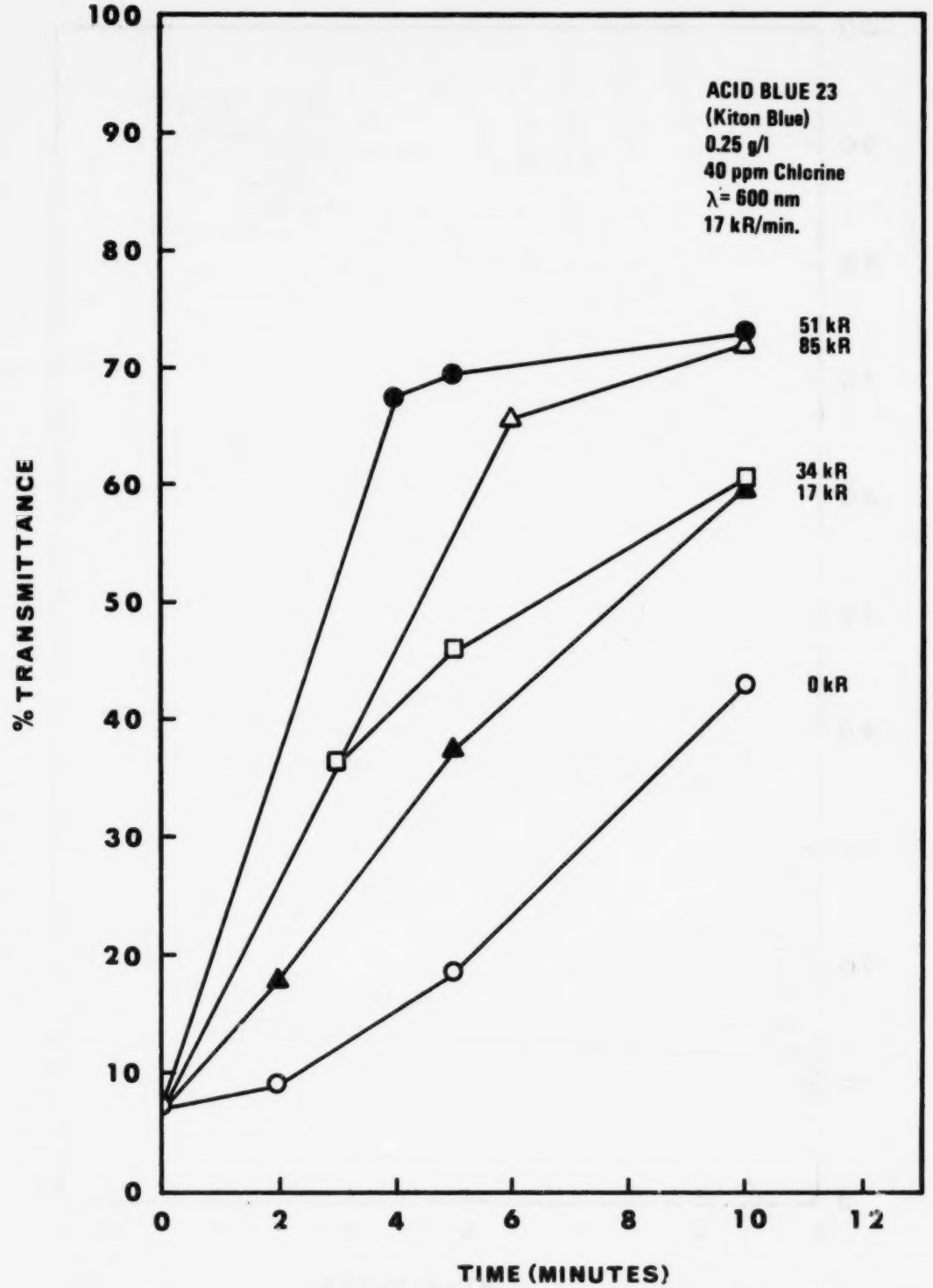

Figure 3 Transmittance Curves for Acid Blue 23 with 40 ppm Chlorine

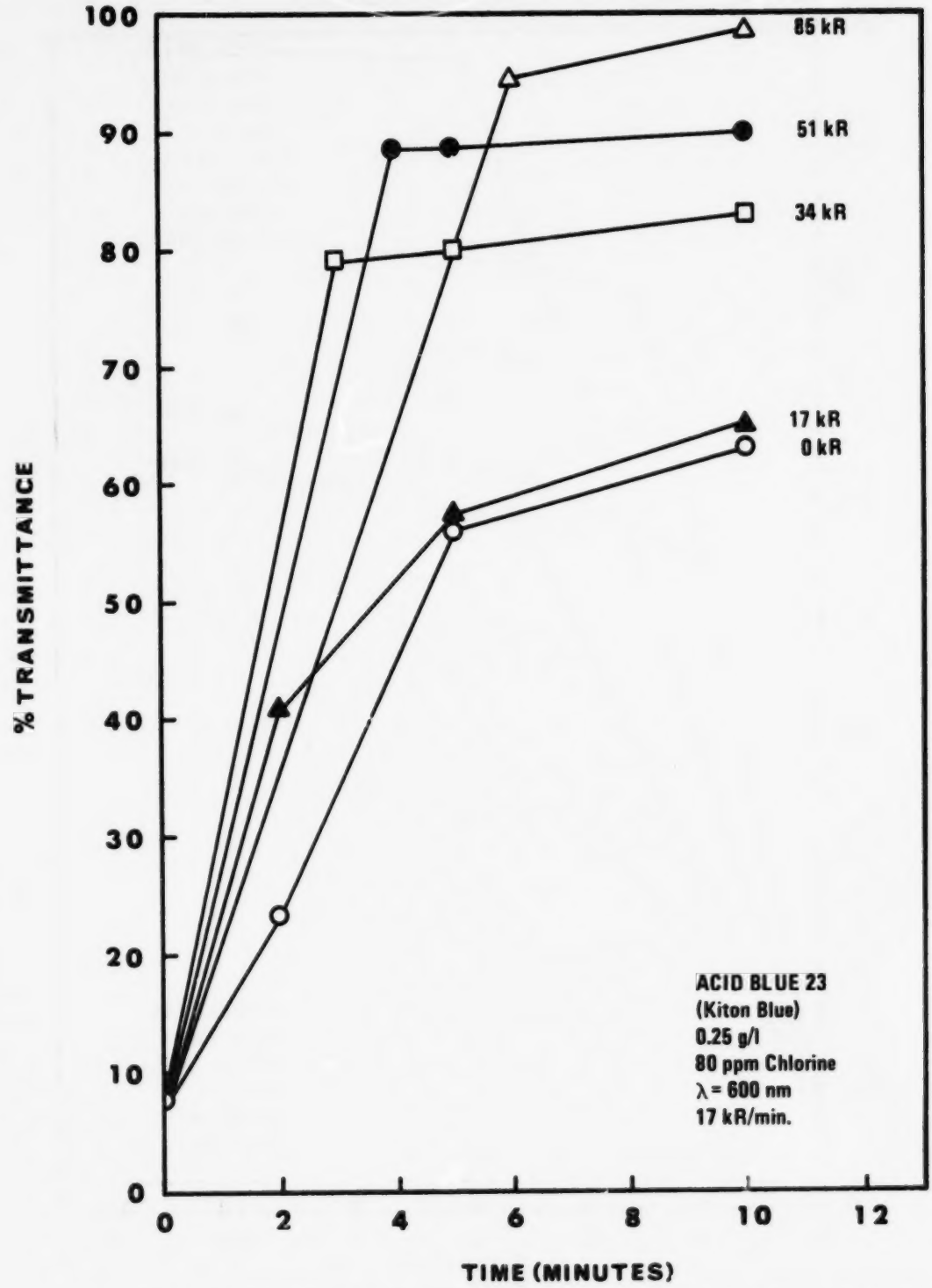

Figure 4 Transmittance Curves for Acid Blue 23 with 80 ppm Chlorine

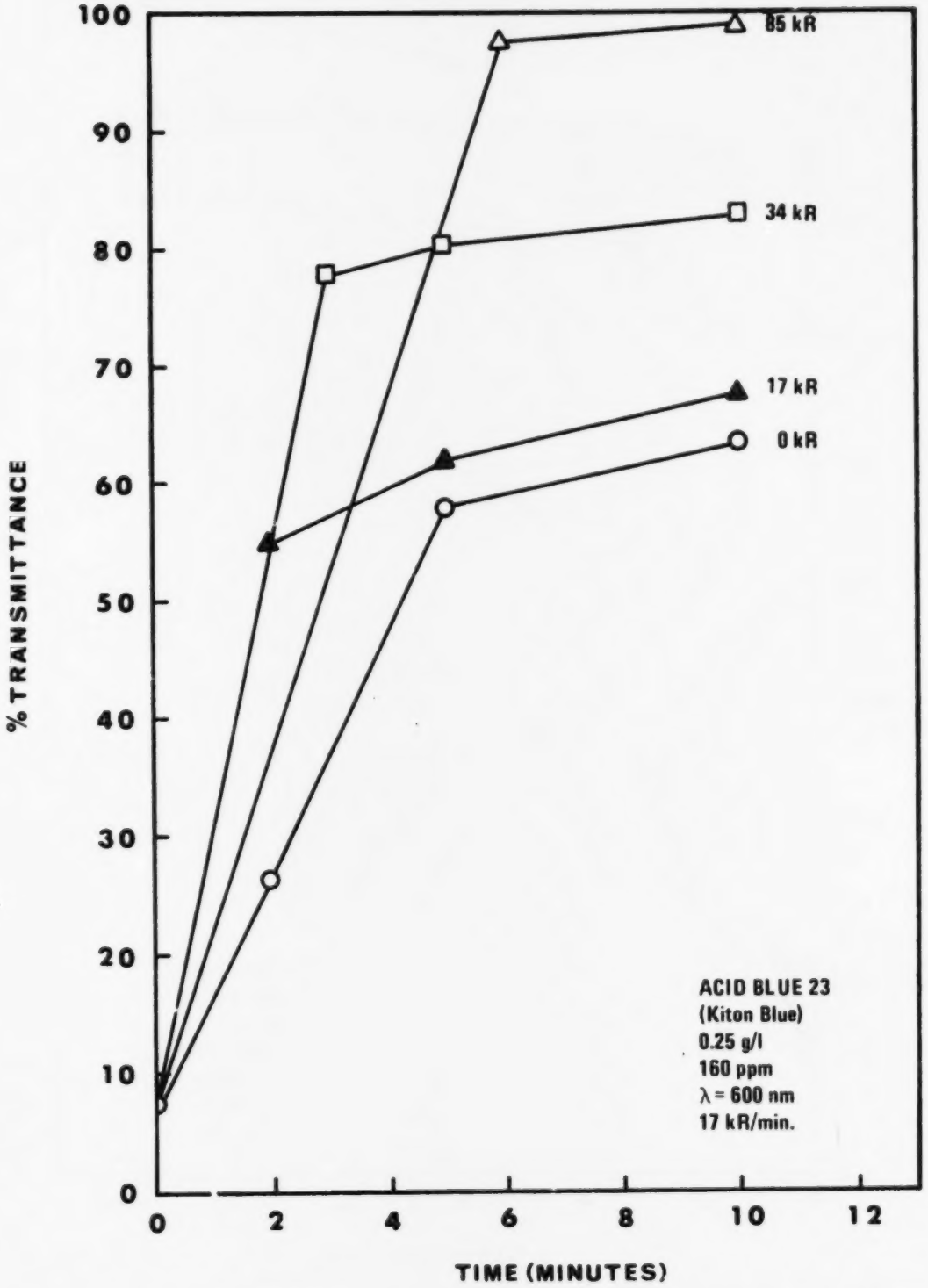

Figure 5 Transmittance Curves for Acid Blue 23 with 160 ppm Chlorine

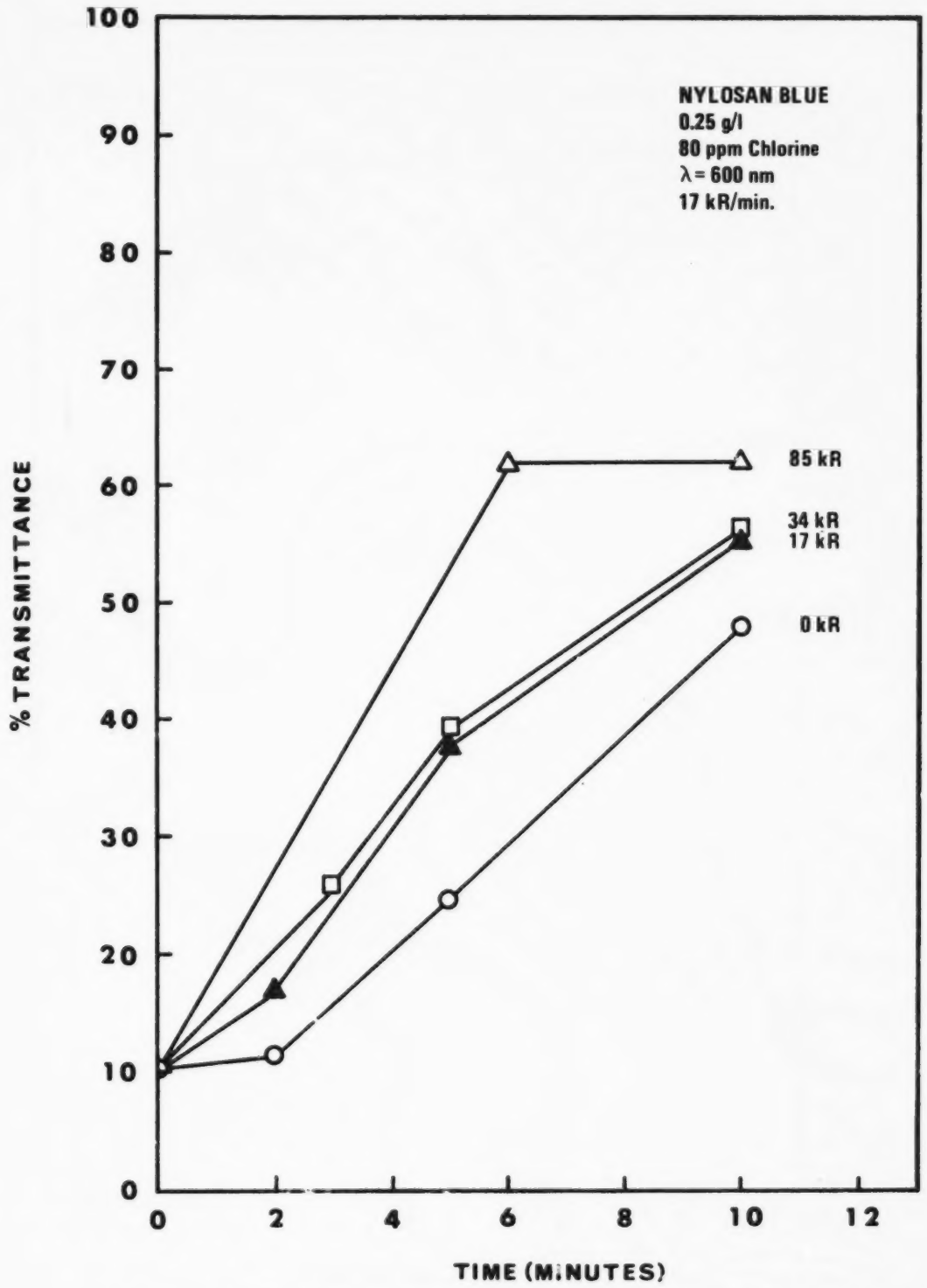

Figure 6 Transmittance Curves for Nylosan Blue with 80 ppm Chlorine

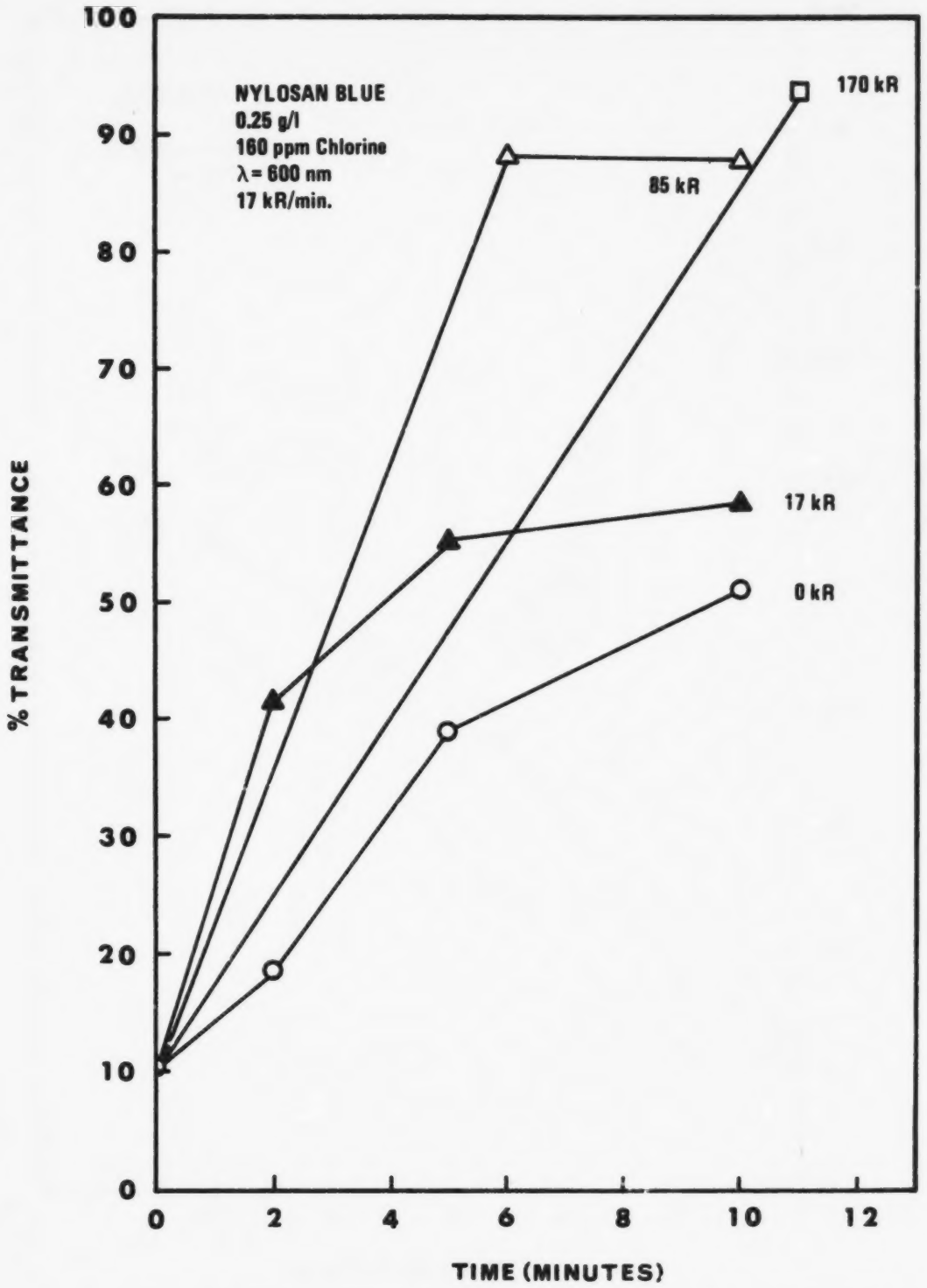

Figure 7 Transmittance Curves for Nylosan Blue with 160 ppm Chlorine

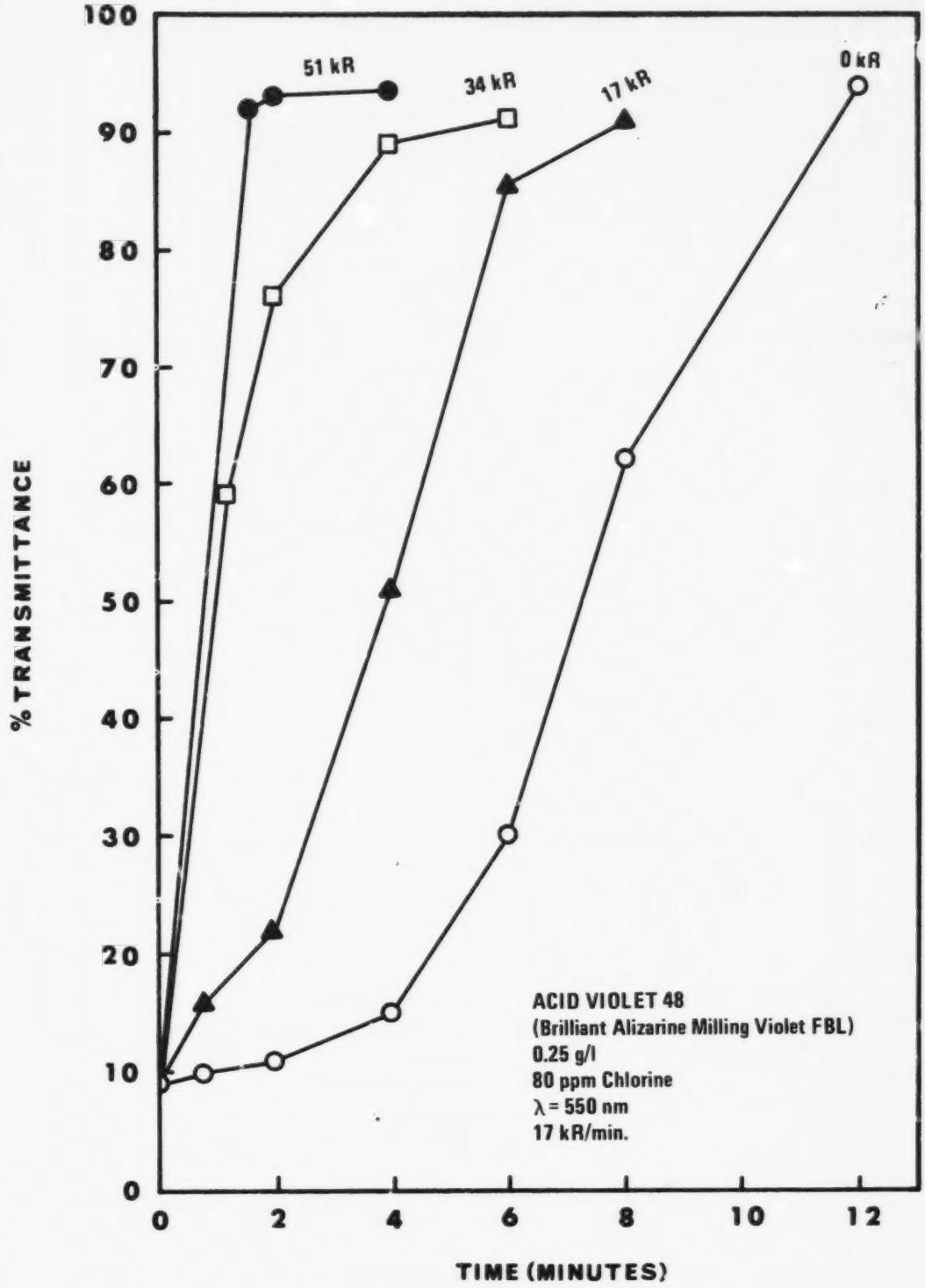

Figure 8 Transmittance Curves for Acid Violet 48 with 80 ppm Chlorine

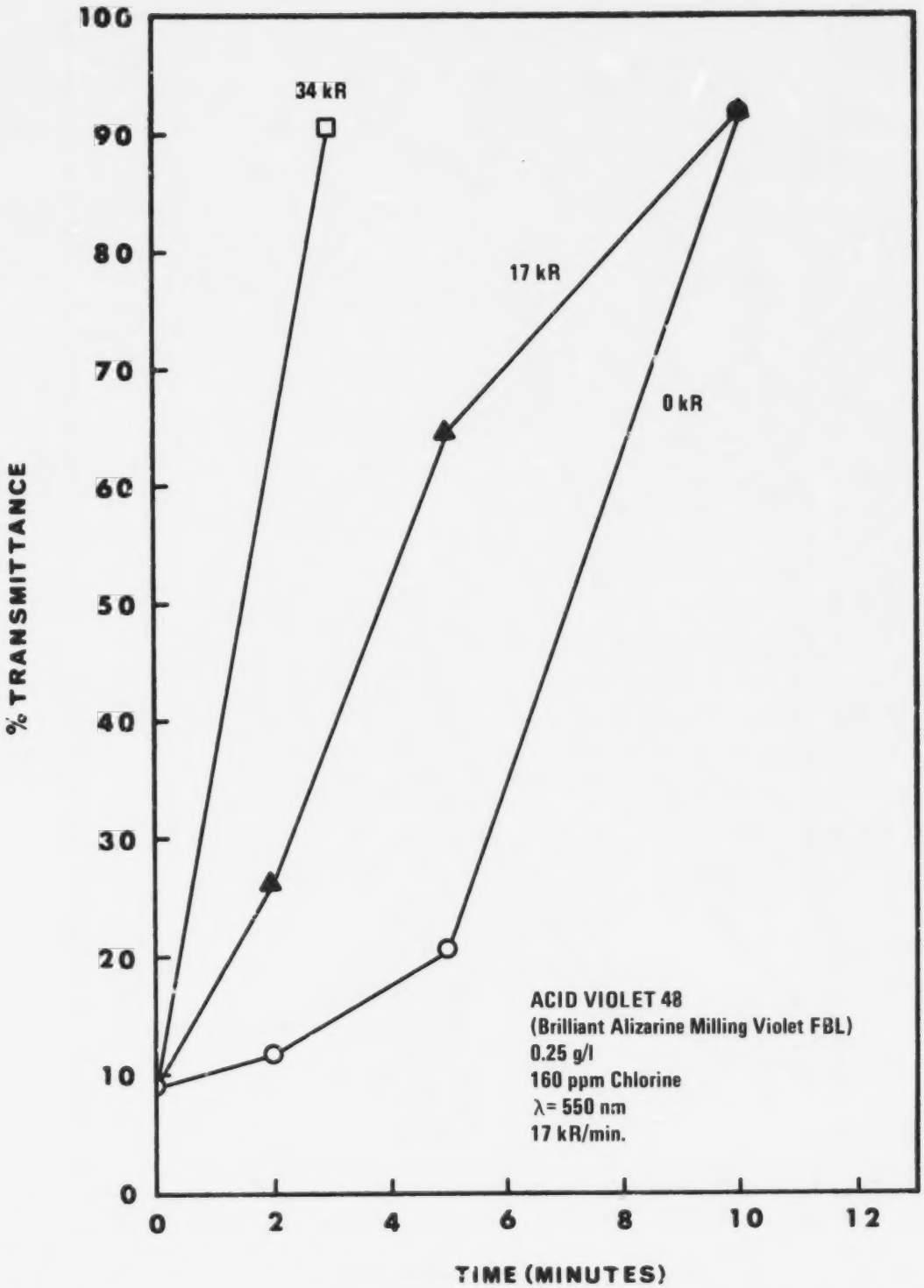

Figure 9 Transmittance Curves for Acid Violet 48 with 160 ppm Chlorine

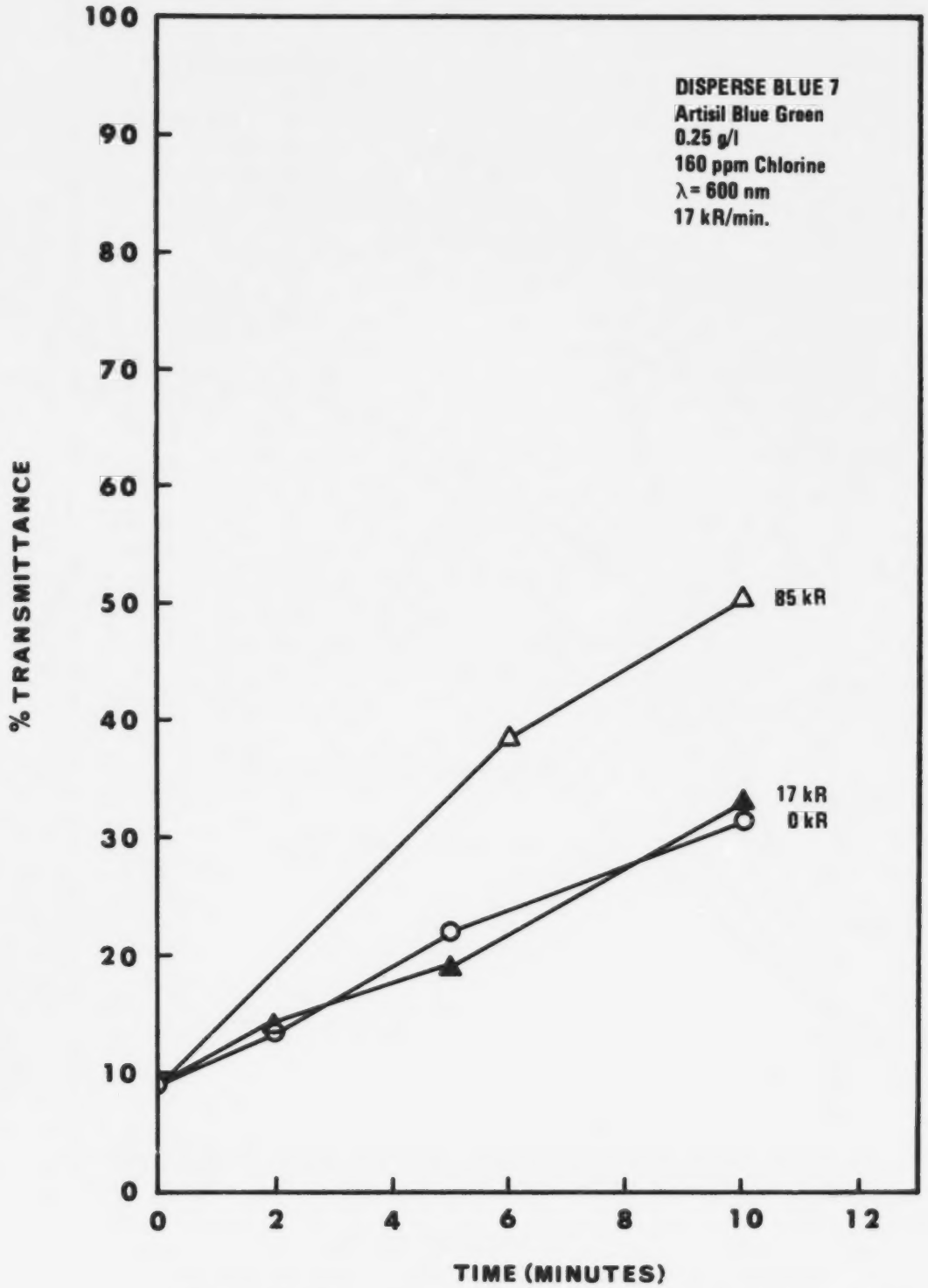

Figure 10 Transmittance Curves for Disperse Blue 7

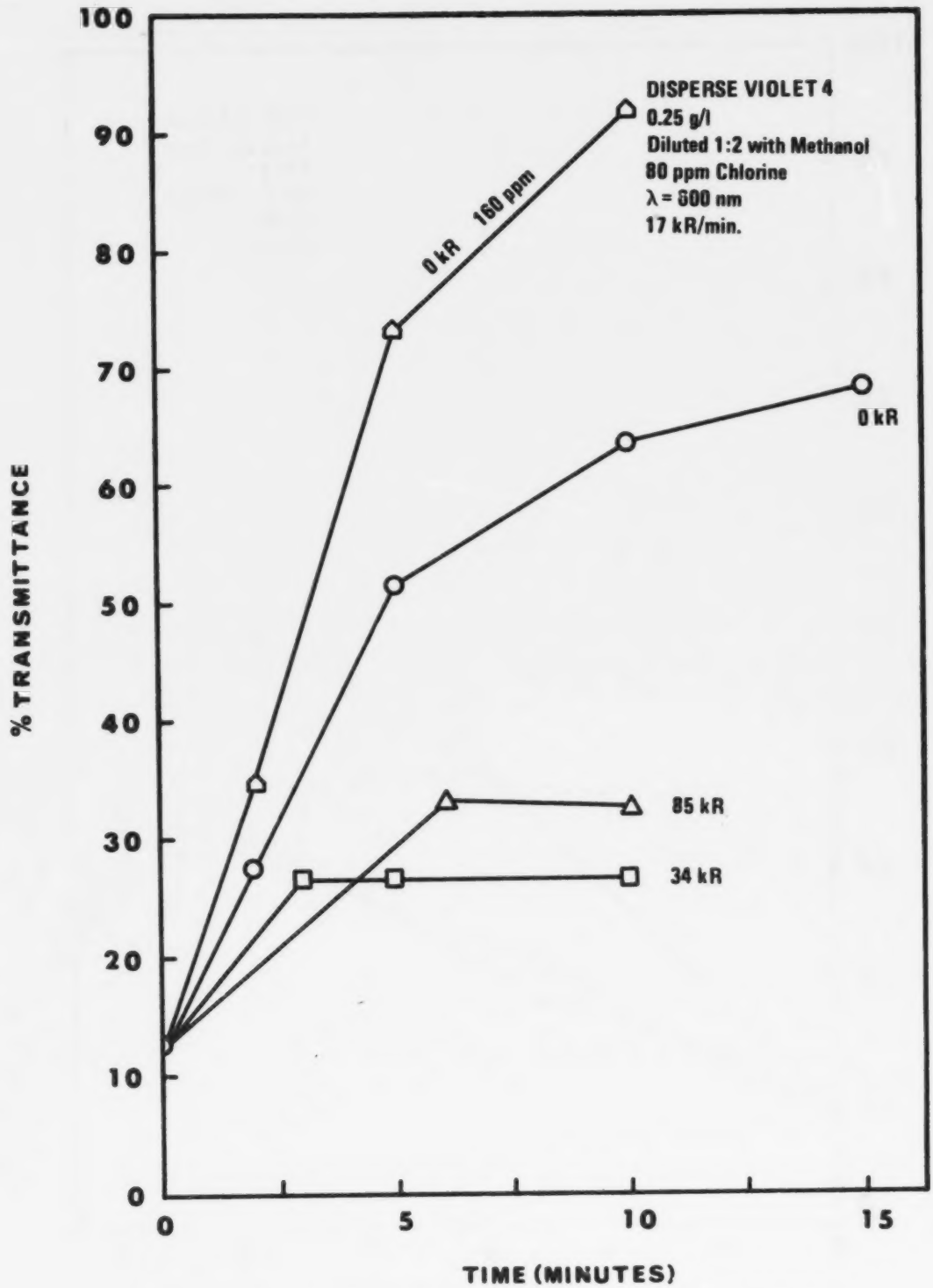

Figure 11 Transmittance Curves for Disperse Violet 4 with 80 ppm Chlorine (Methanol)

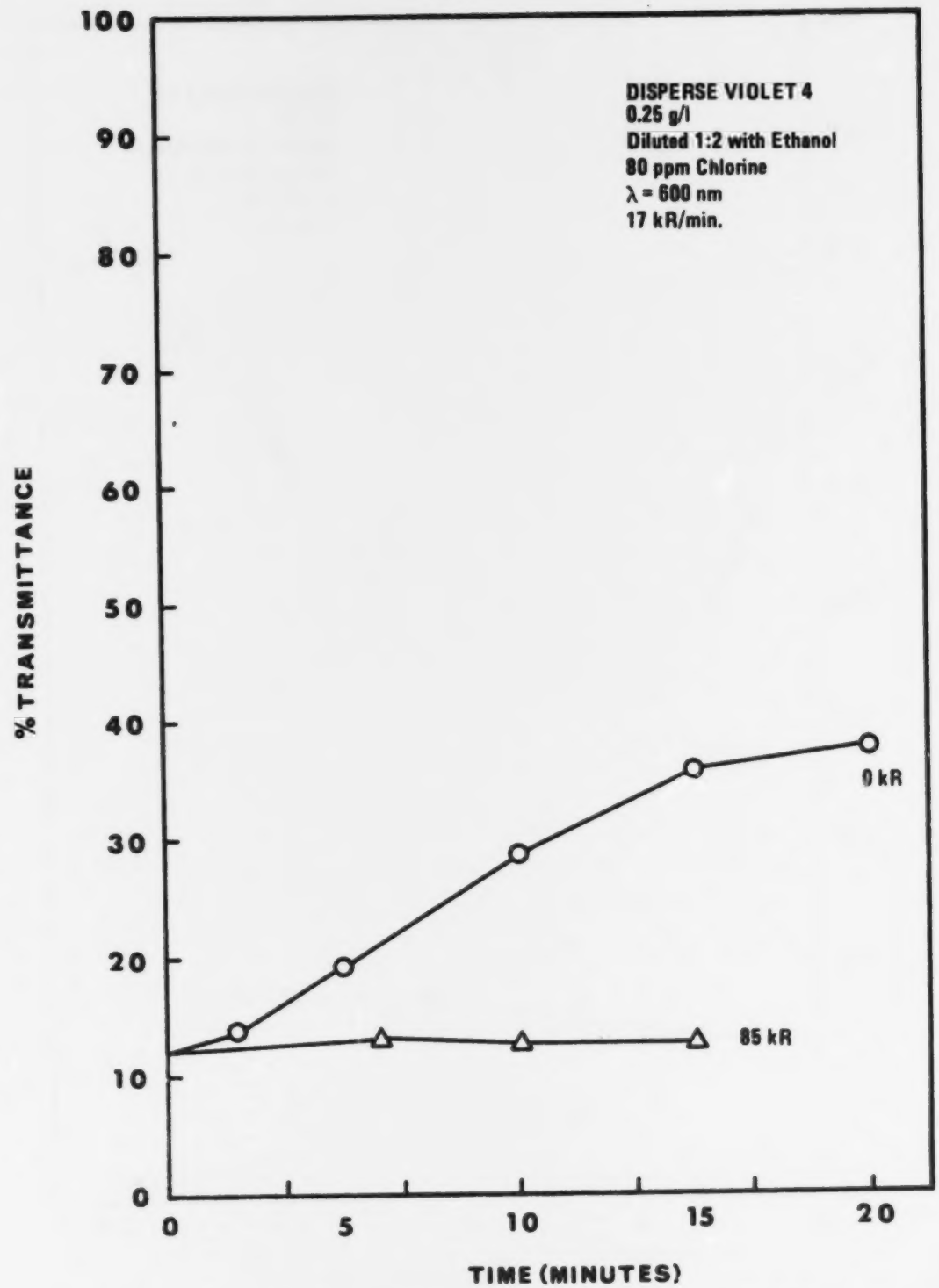

Figure 12 Transmittance Curves for Disperse Violet 4 with 80 ppm Chlorine (Ethanol)

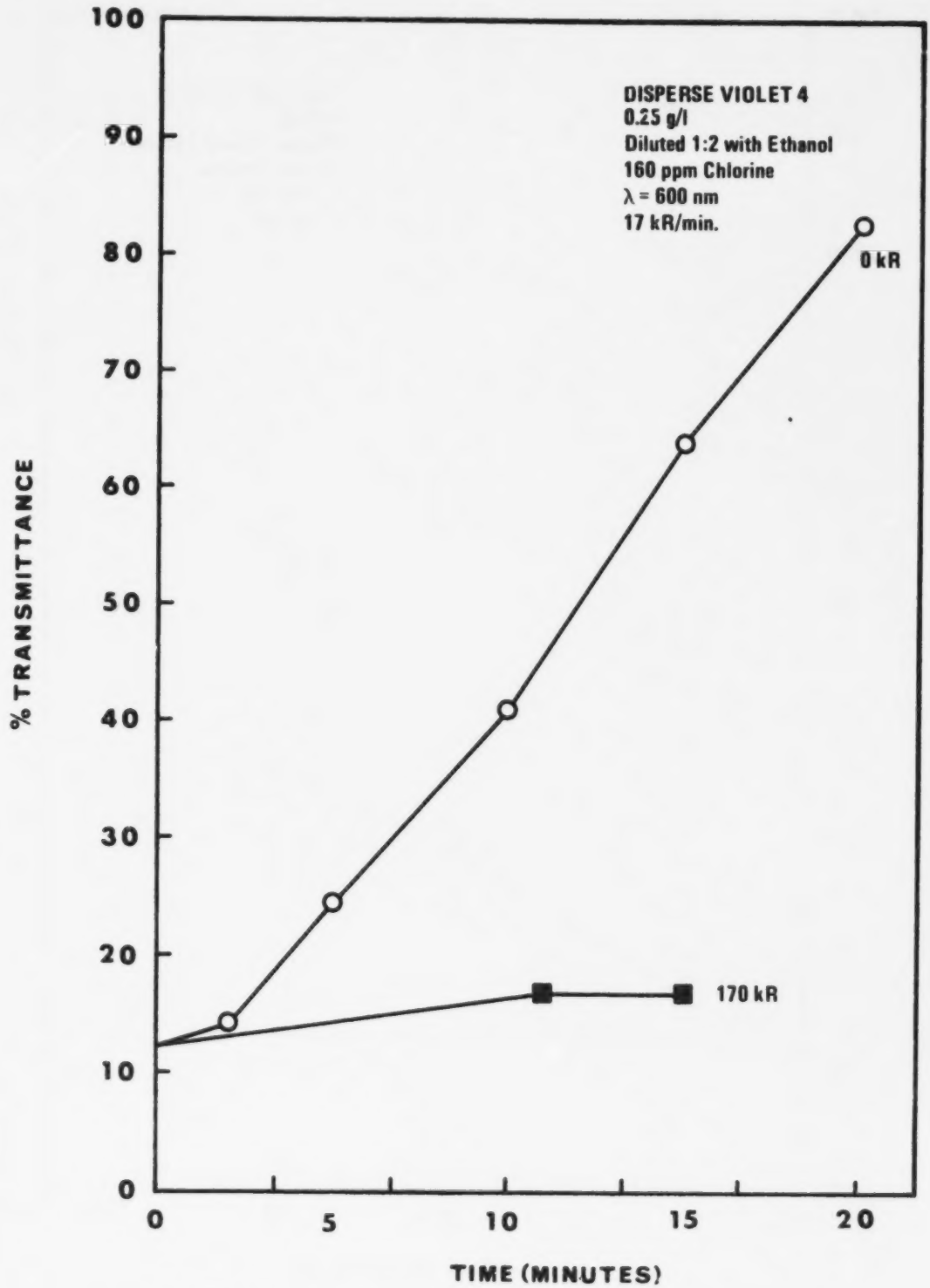

Figure 13 Transmittance Curves for Disperse Violet 4 with 160 ppm Chlorine (Ethanol)

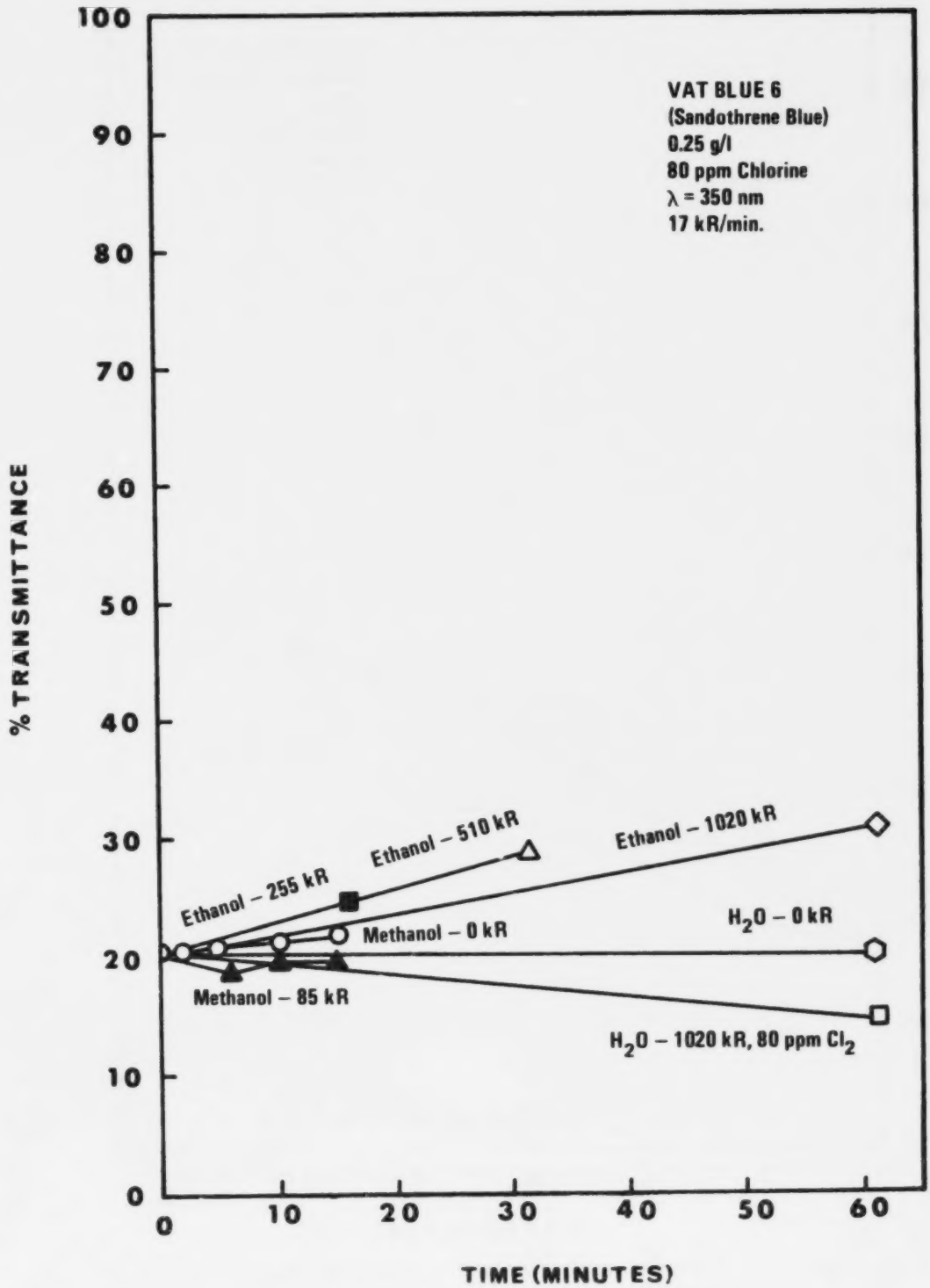

Figure 14 Transmittance Curves for Vat Blue 6

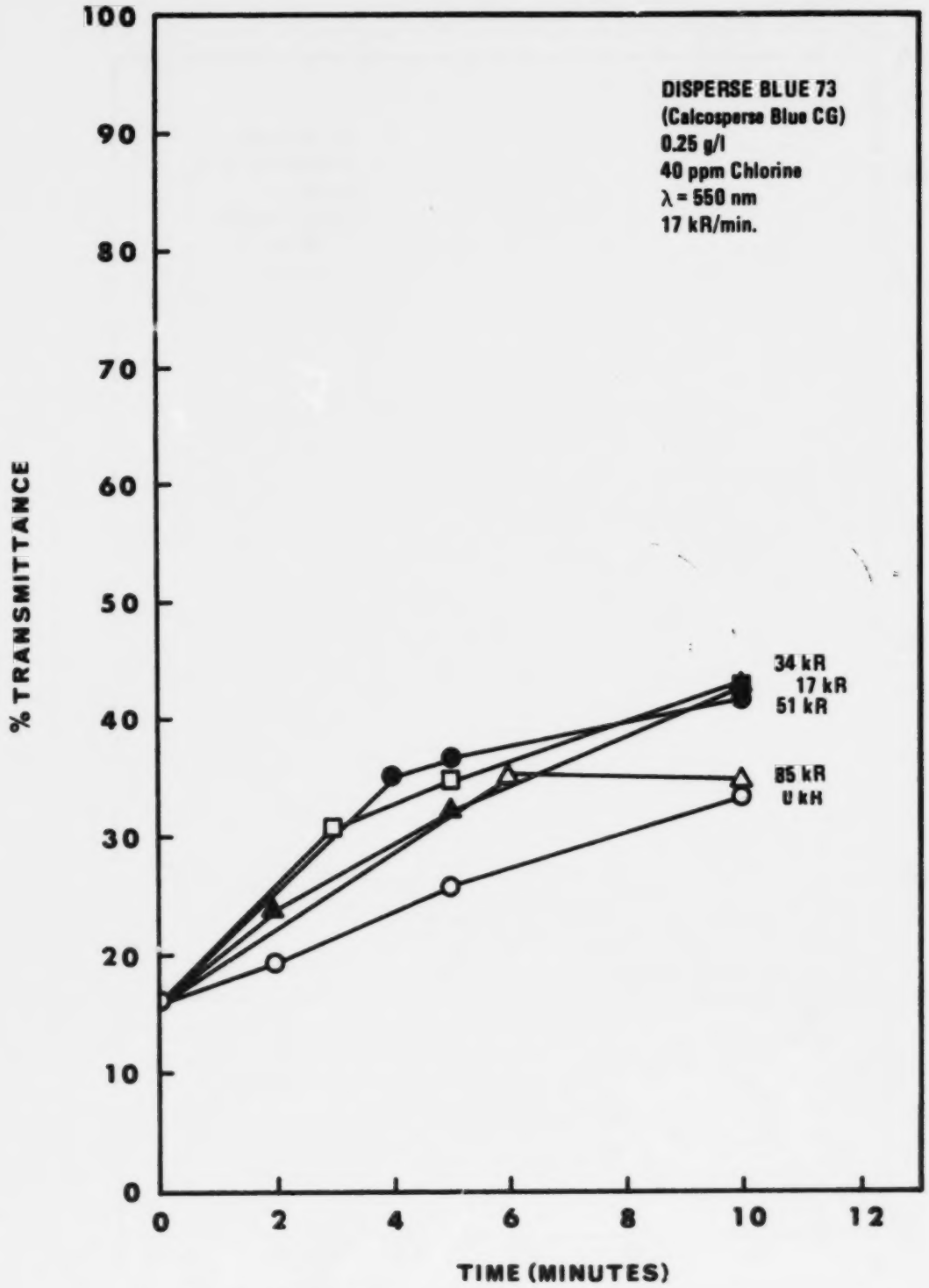

Figure 15 Transmittance Curves for Disperse Blue 73 with 40 ppm Chlorine

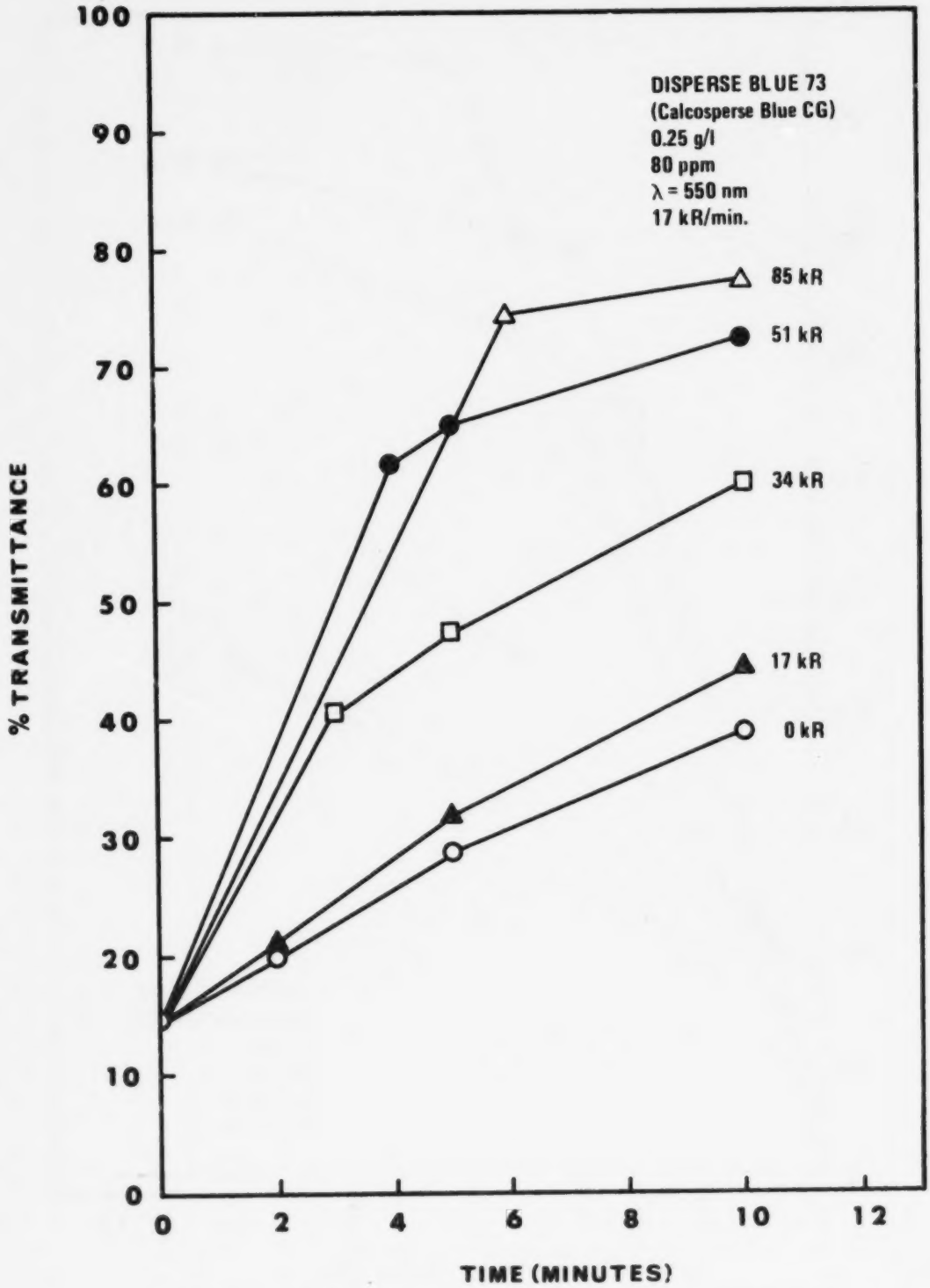

Figure 16 Transmittance Curves for Disperse Blue 73 with 80 ppm Chlorine

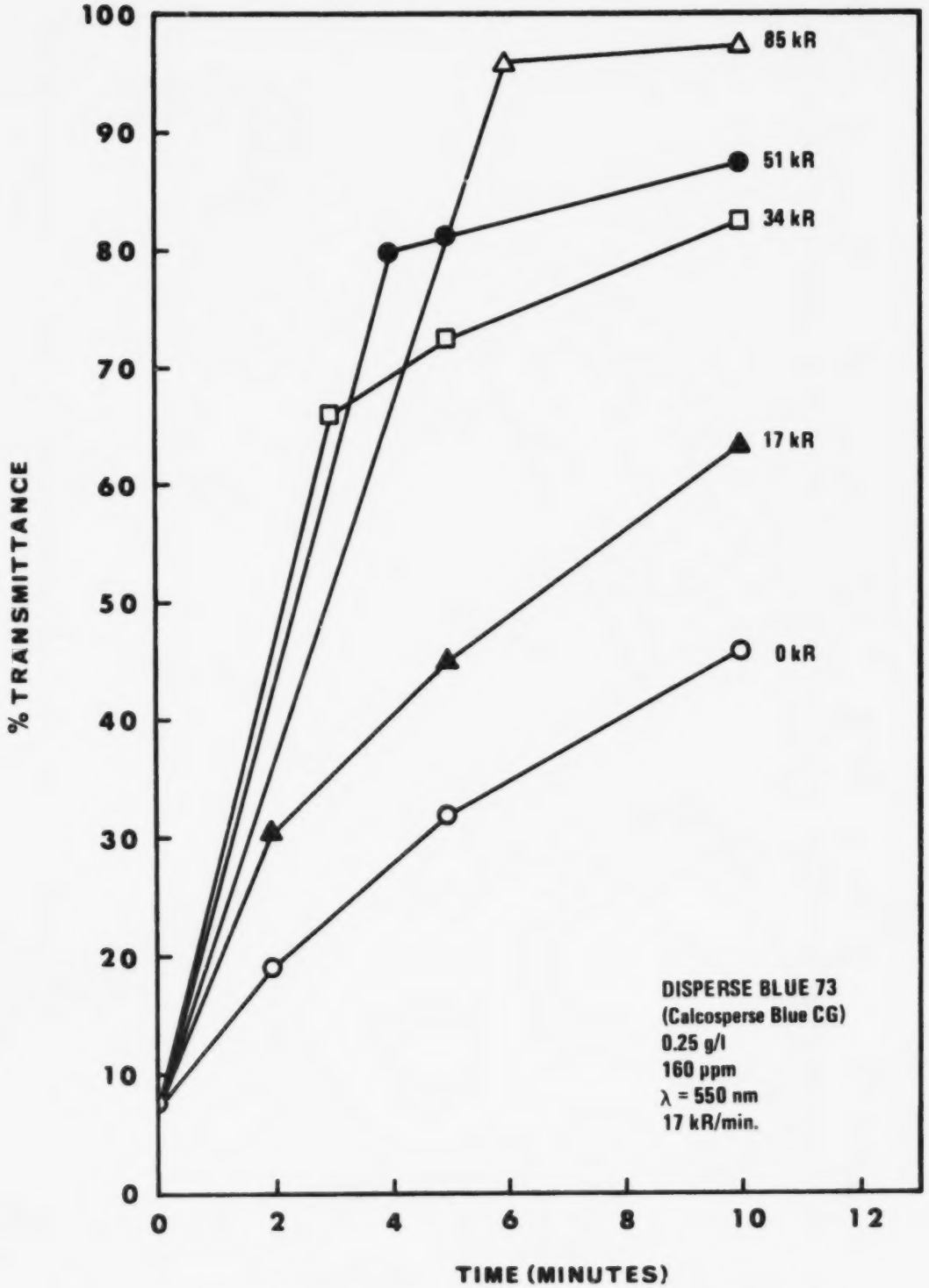

Figure 17 Transmittance Curves for Disperse Blue 73 with 160 ppm Chlorine

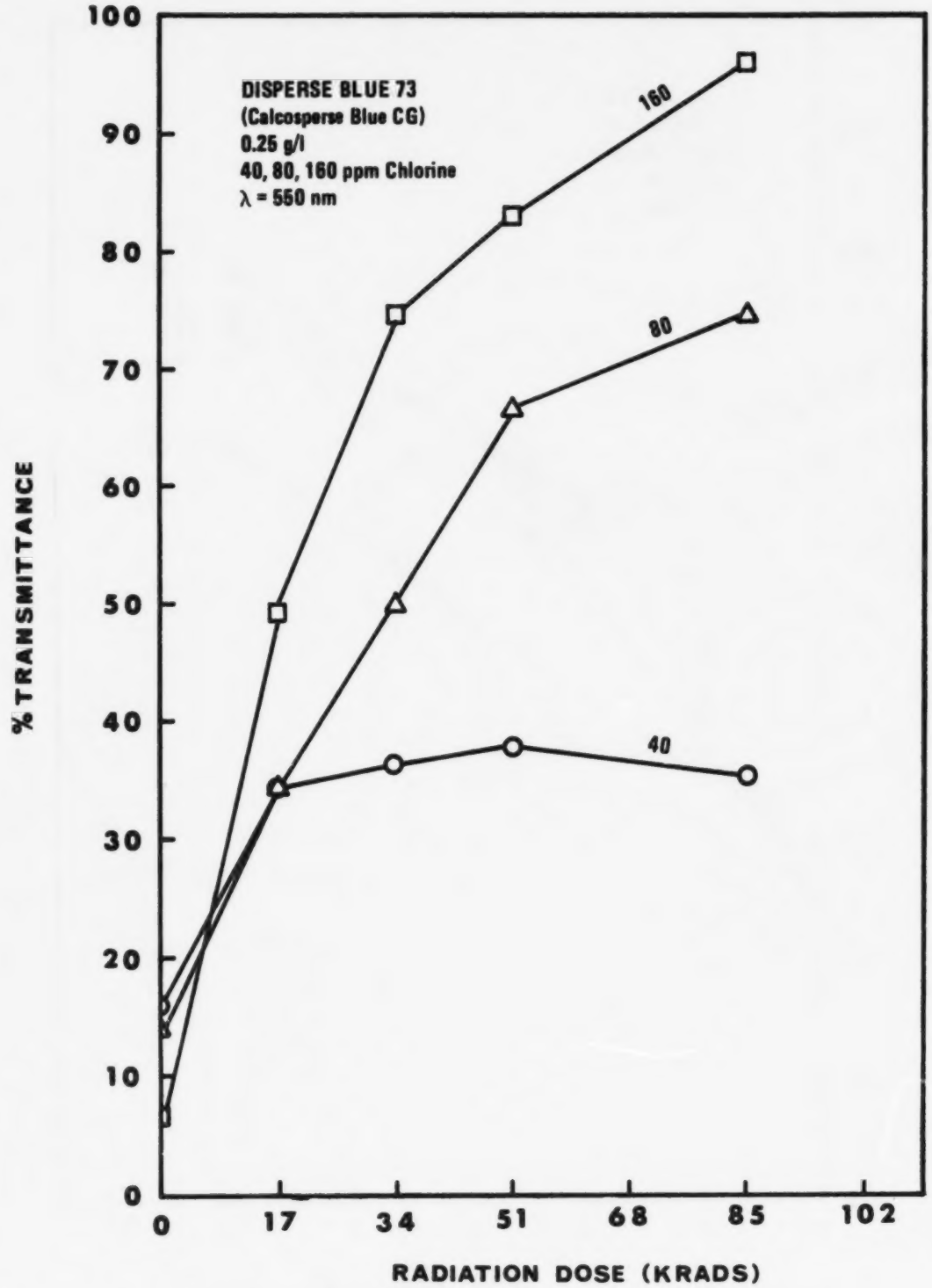

Figure 18 Transmittance Curves for Disperse Blue 73 with 40, 80, 160 ppm Chlorine

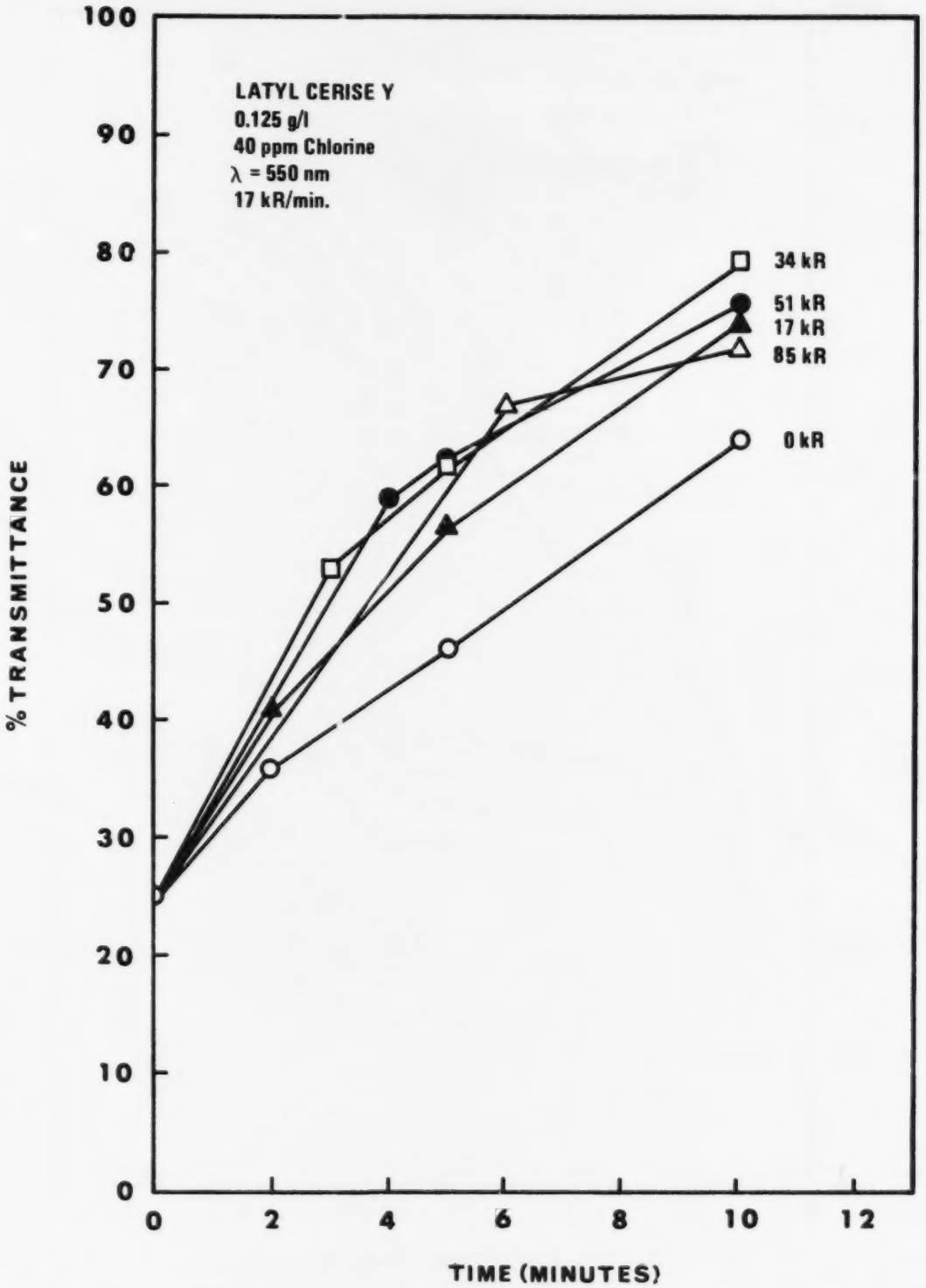

Figure 19 Transmittance Curves for Latyl Cerise Y with 40 ppm Chlorine

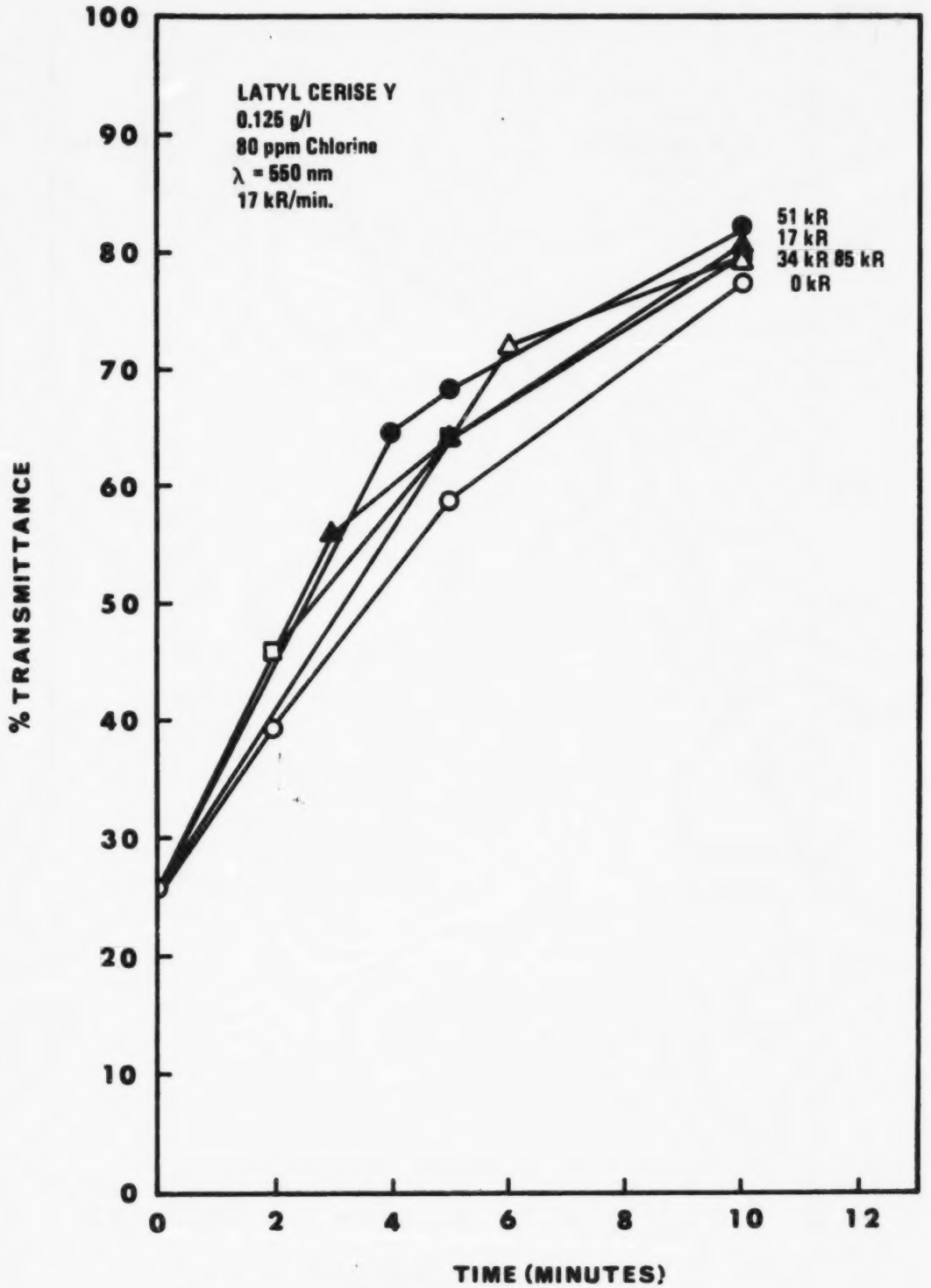

Figure 20 Transmittance Curves for Latyl Cerise Y with 80 ppm Chlorine

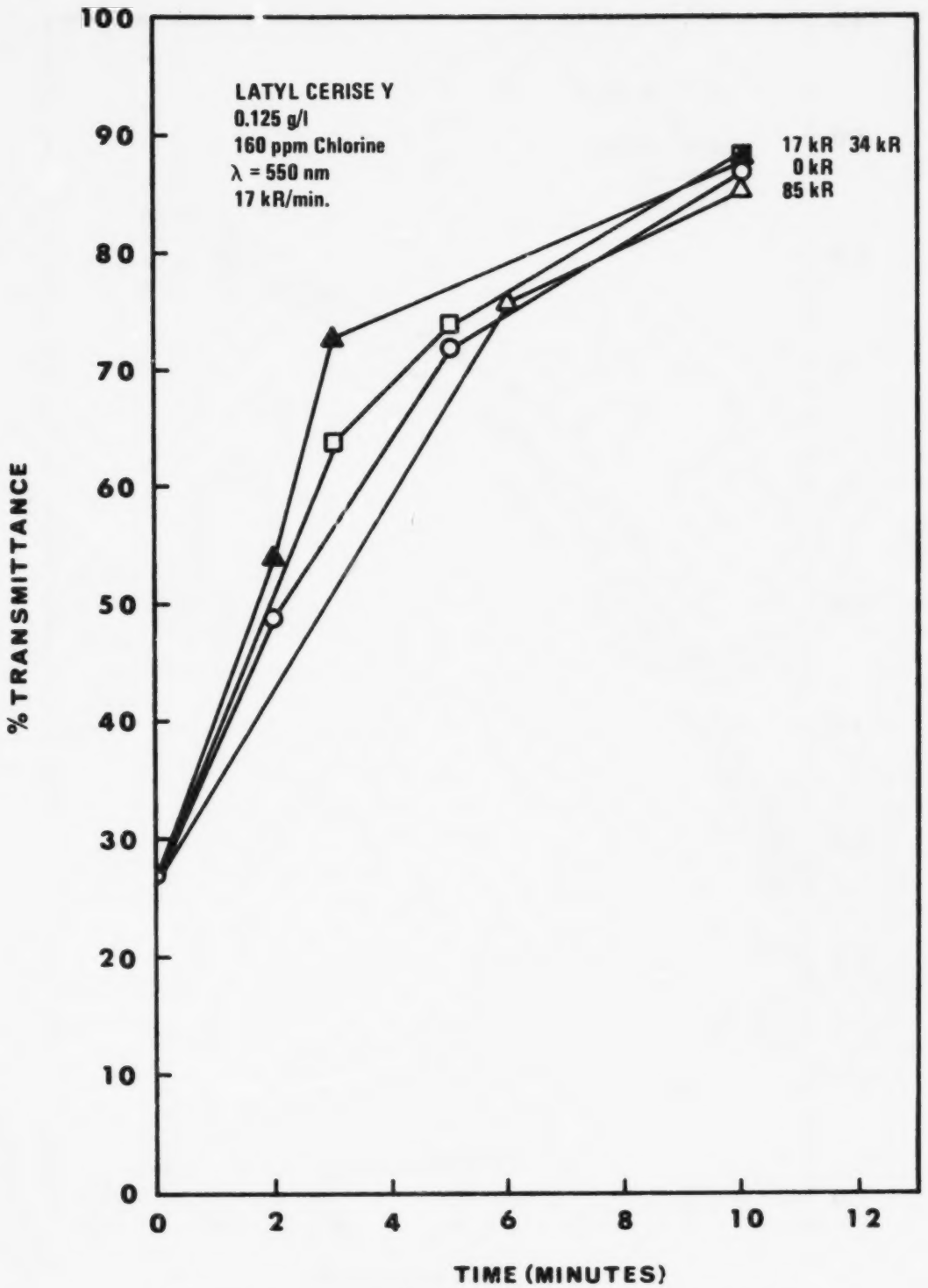

Figure 21 Transmittance Curves for Latyl Cerise Y with 160 ppm Chlorine

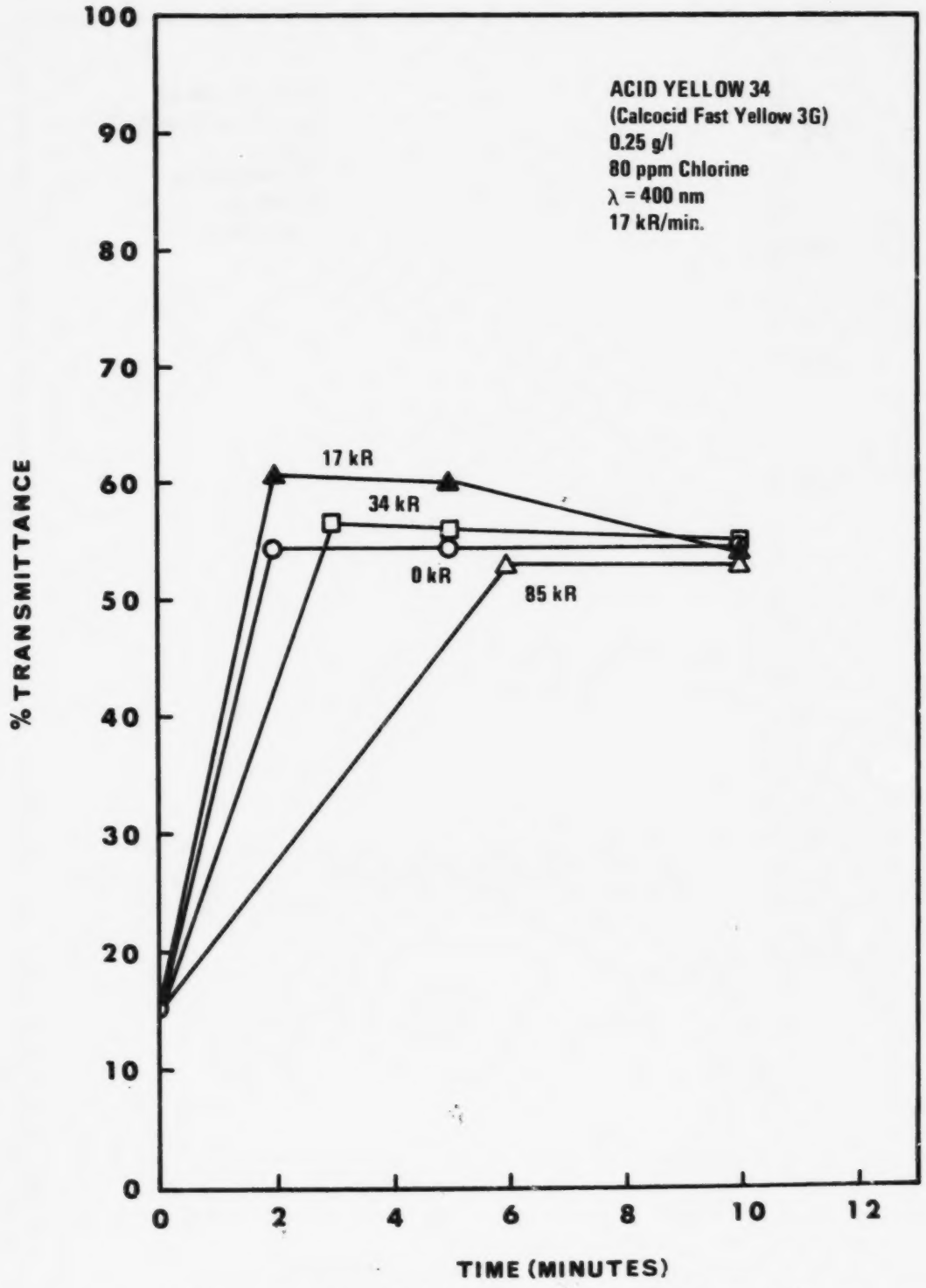

Figure 22 Transmittance Curves for Acid Yellow 34

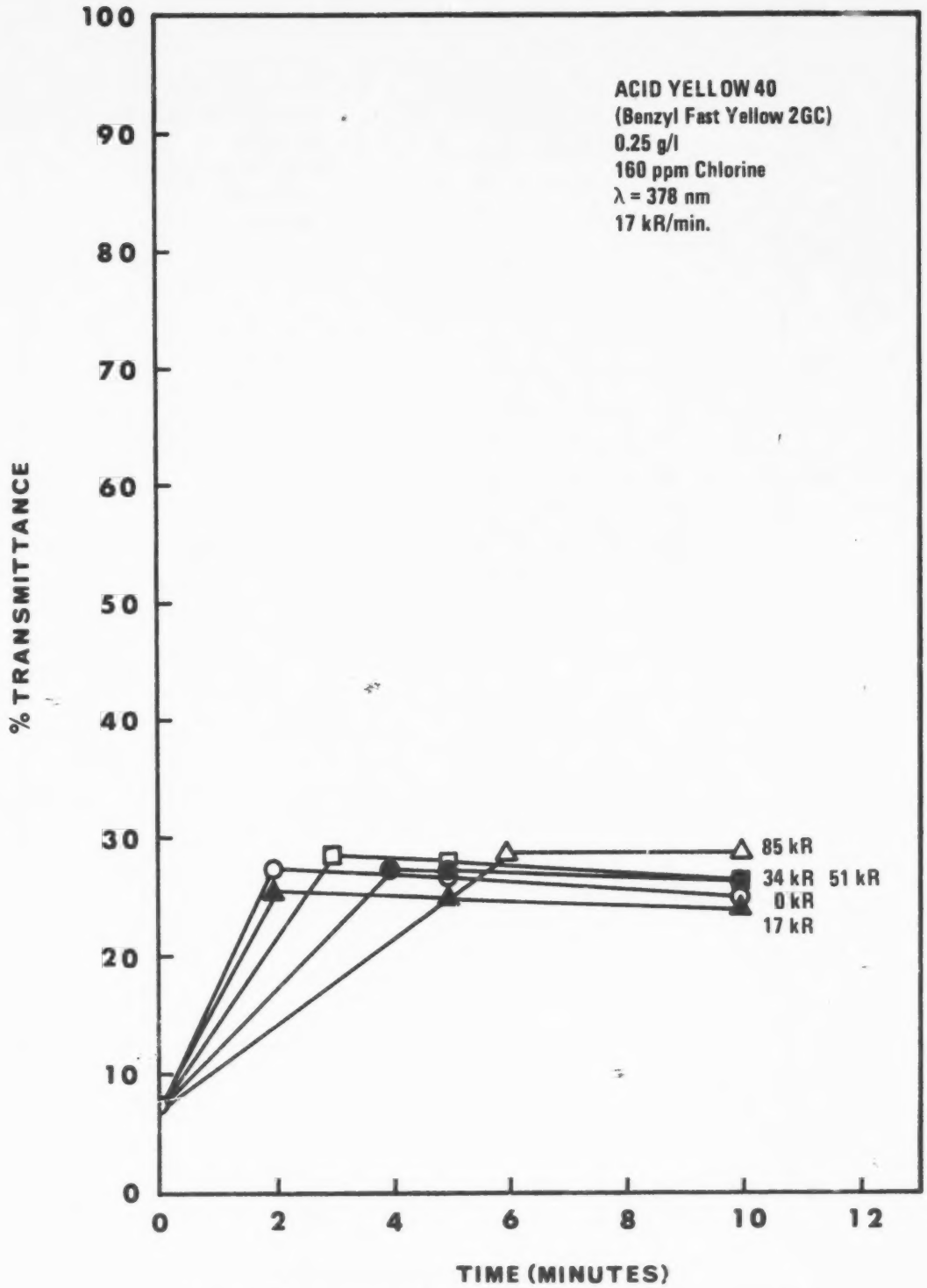

Figure 23 Transmittance Curves for Acid Yellow 40 with 160 ppm Chlorine

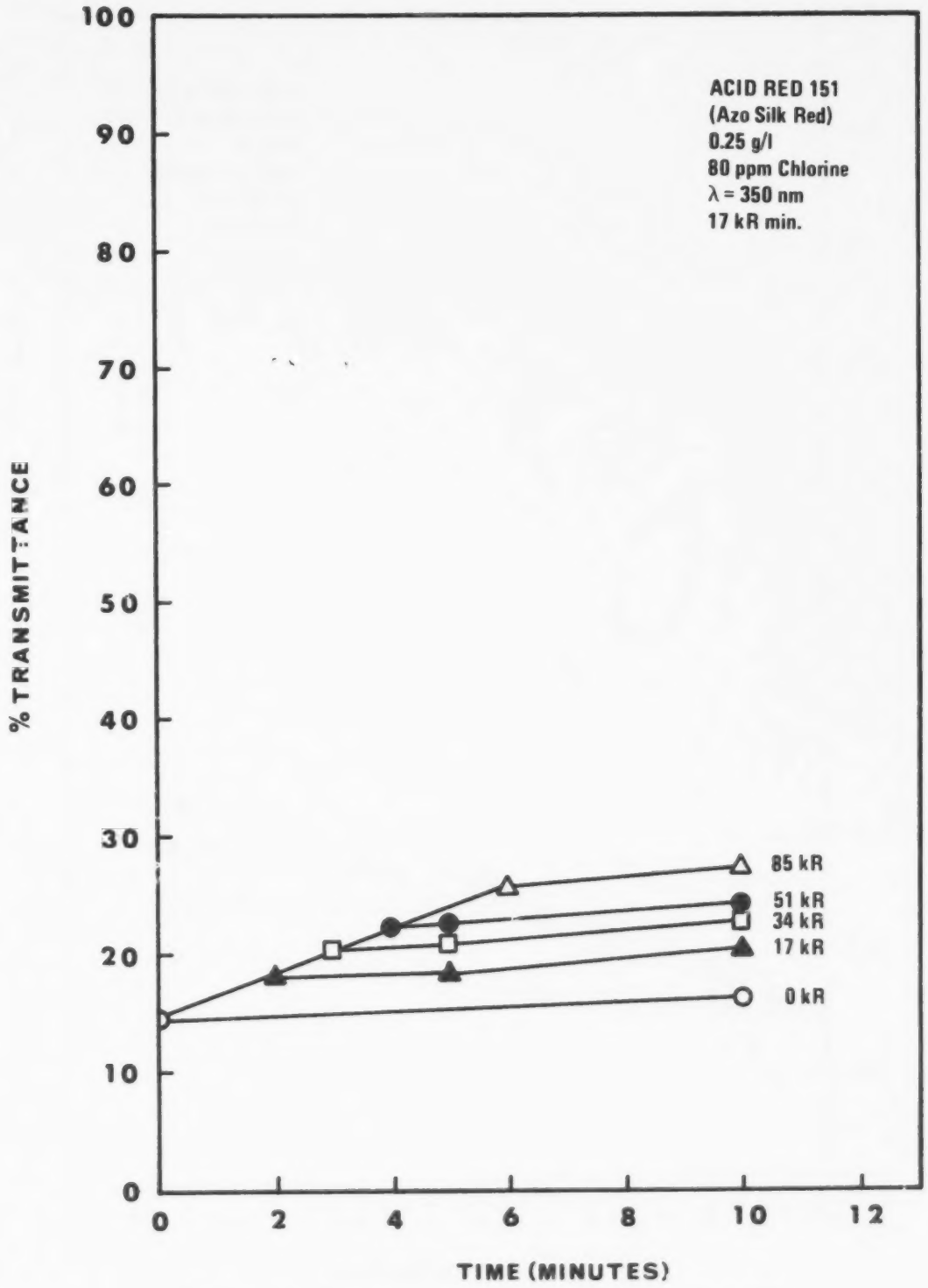

Figure 24 Transmittance Curves for Acid Red 151 with 80 ppm Chlorine

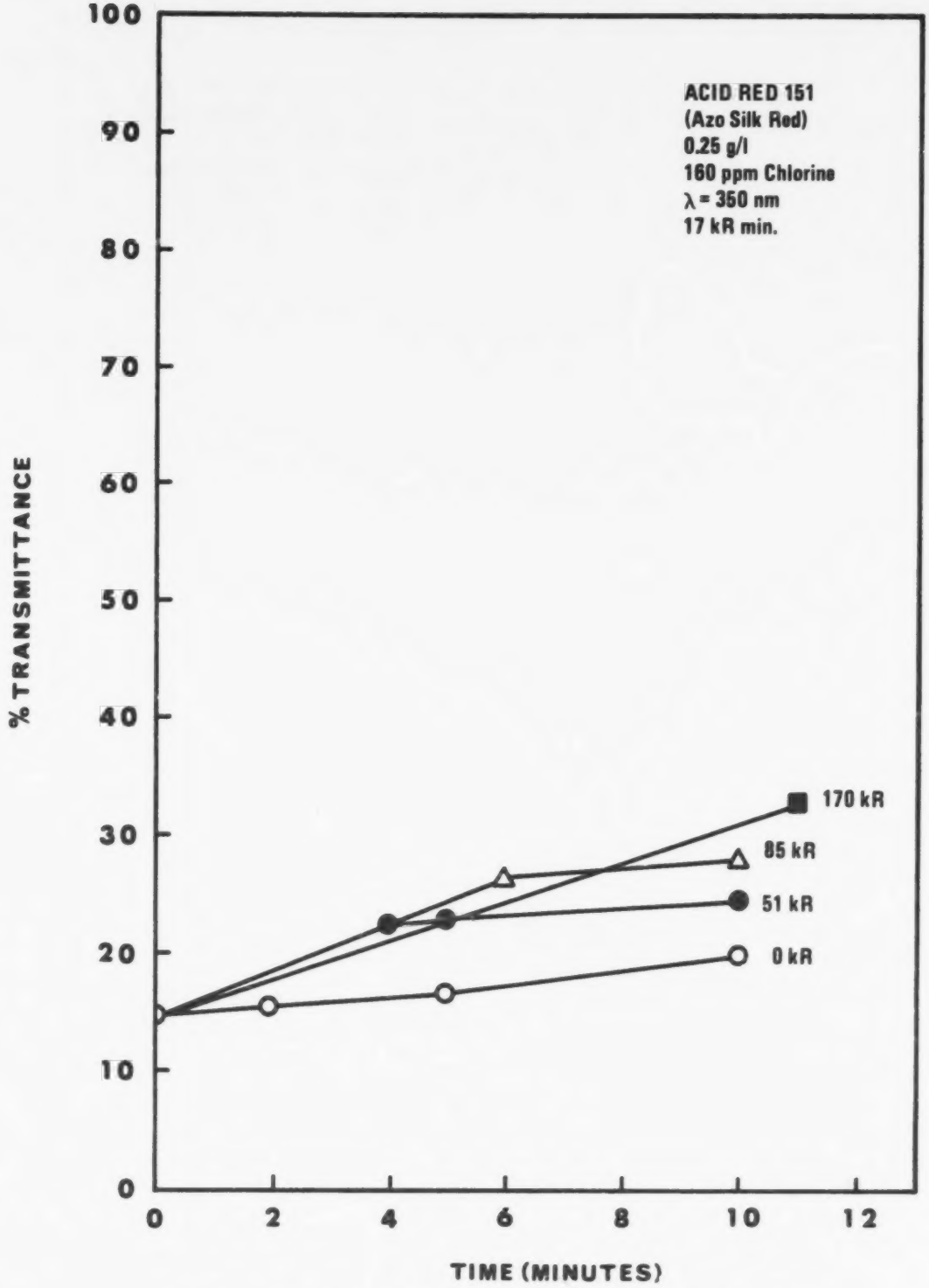

Figure 25 Transmittance Curves for Acid Red 151 with 160 ppm Chlorine

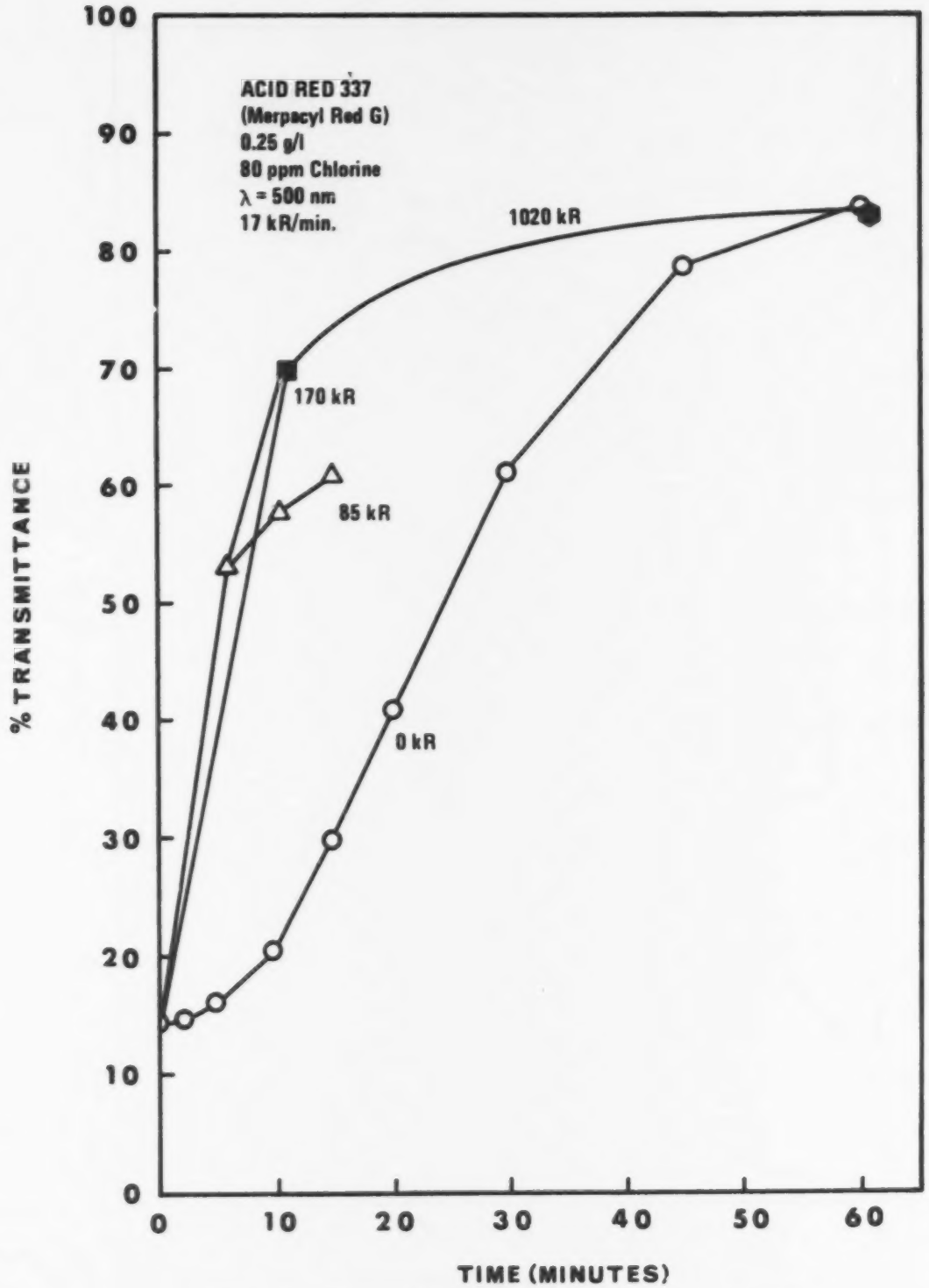

Figure 26 Transmittance Curves for Acid Red 337 with 80 ppm Chlorine

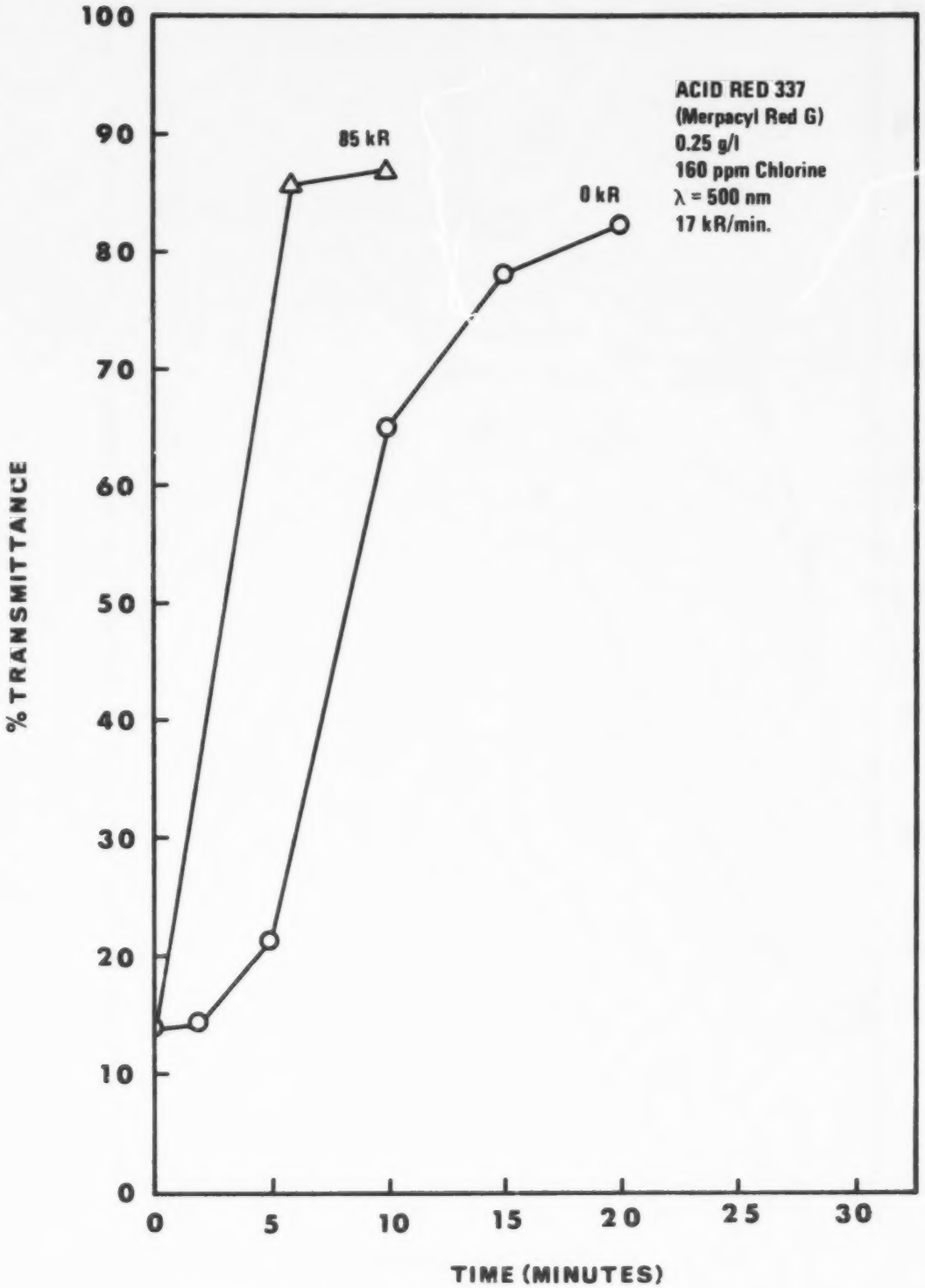

Figure 27 Transmittance Curves for Acid Red 337 with 160 ppm Chlorine

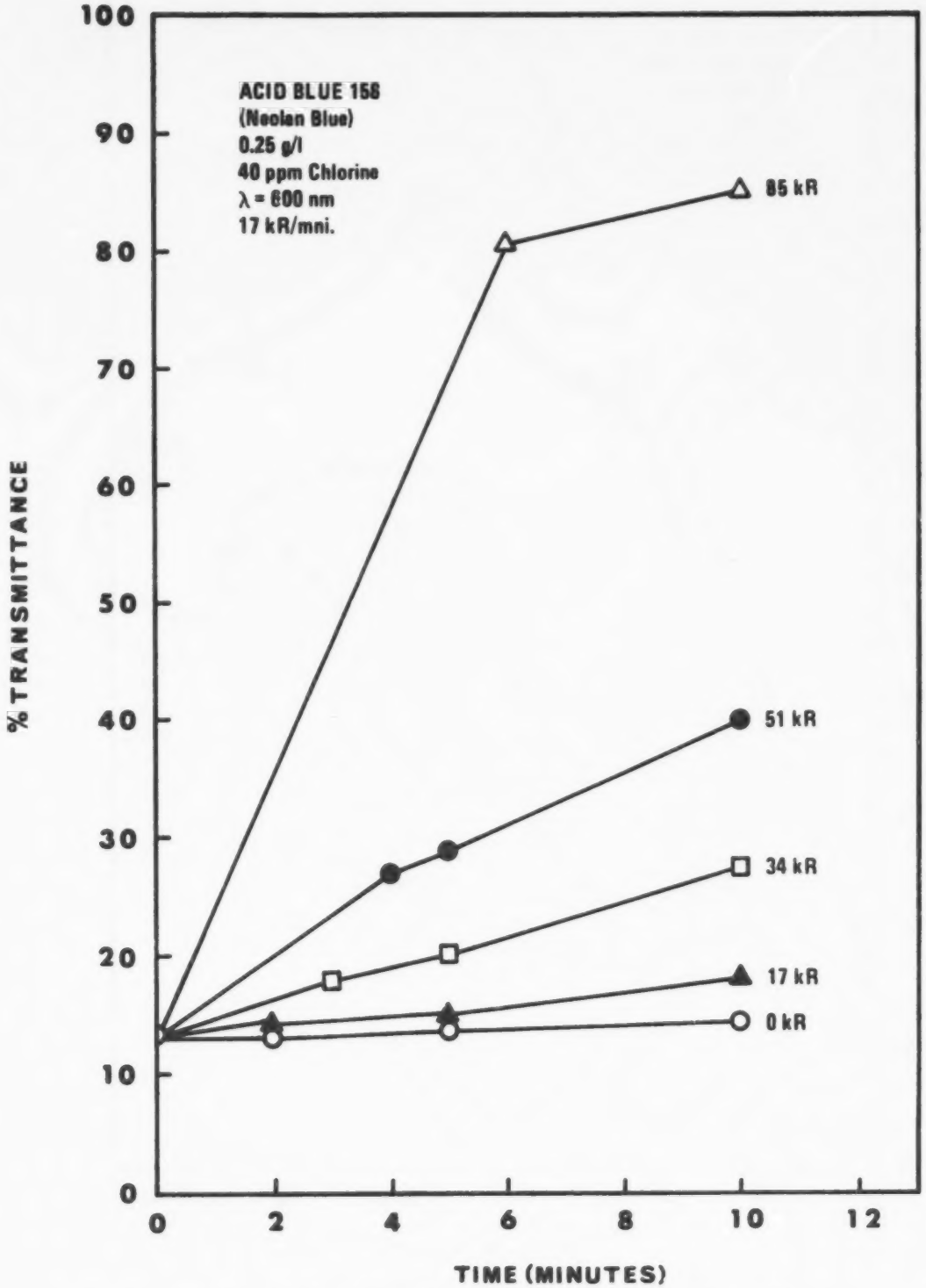

Figure 28 Transmittance Curves for Acid Blue 158 with 40 ppm Chlorine

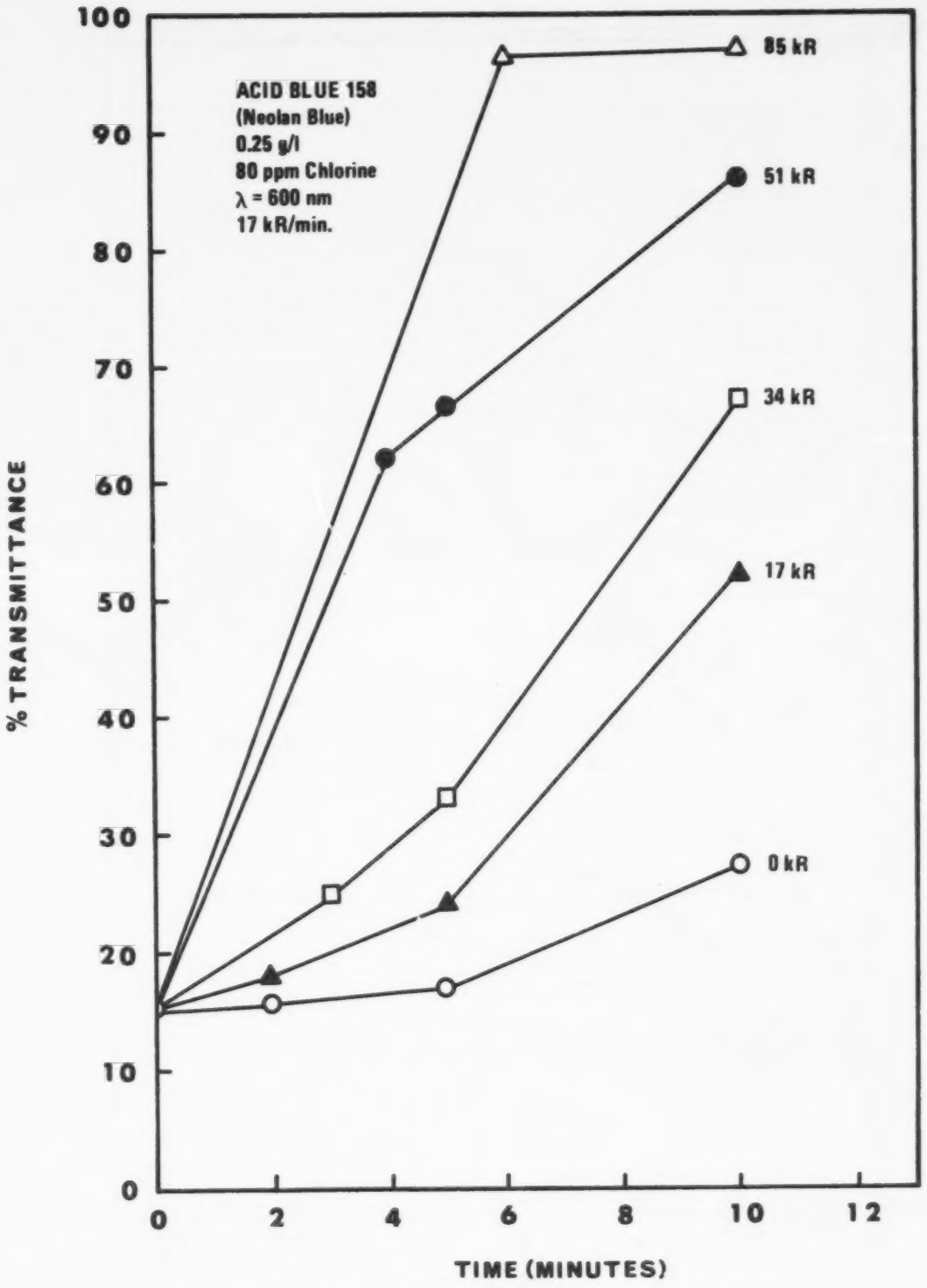

Figure 29 Transmittance Curves for Acid Blue 158 with 80 ppm Chlorine

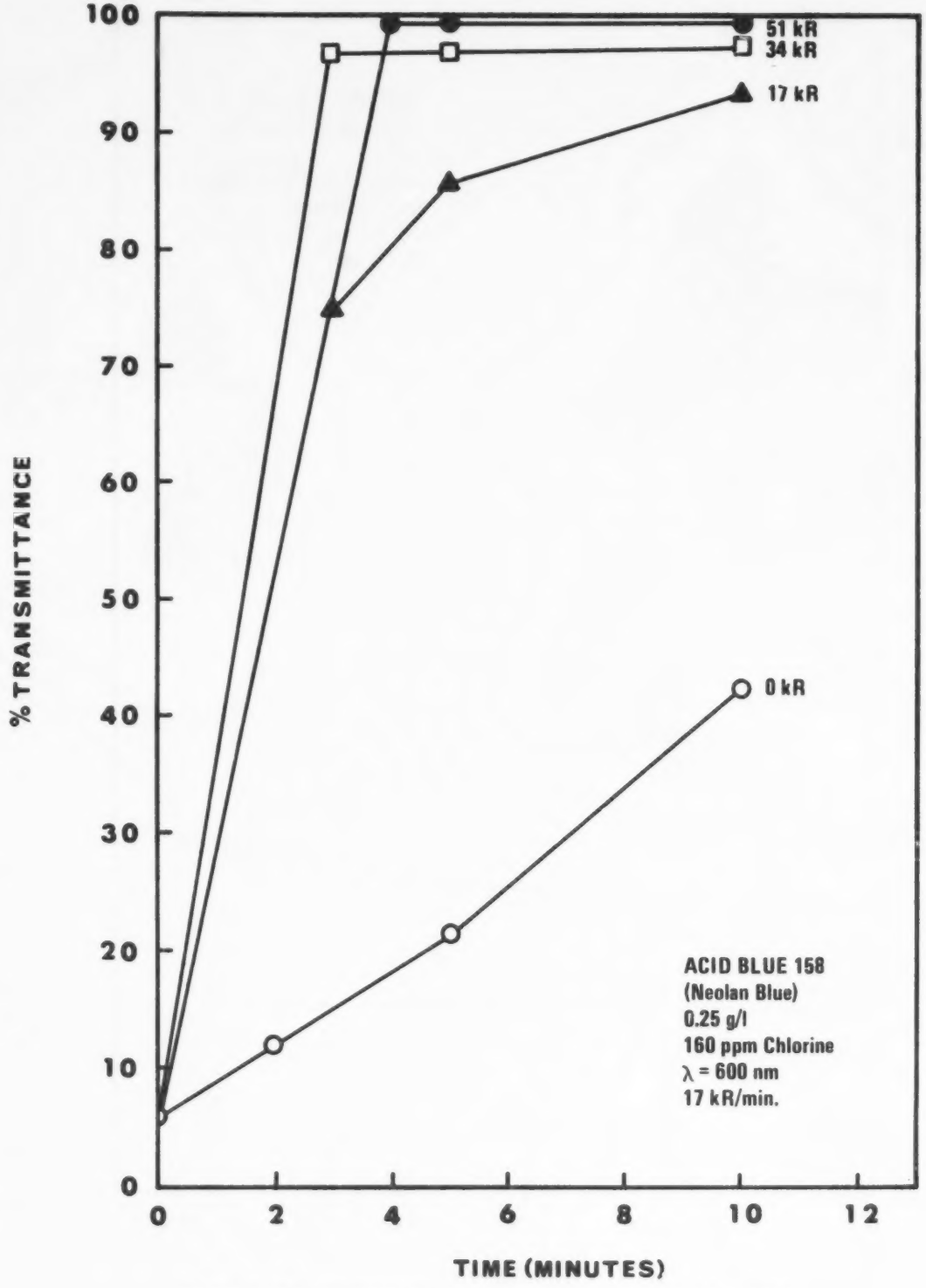

Figure 30 Transmittance Curves for Acid Blue 158 with 160 ppm Chlorine

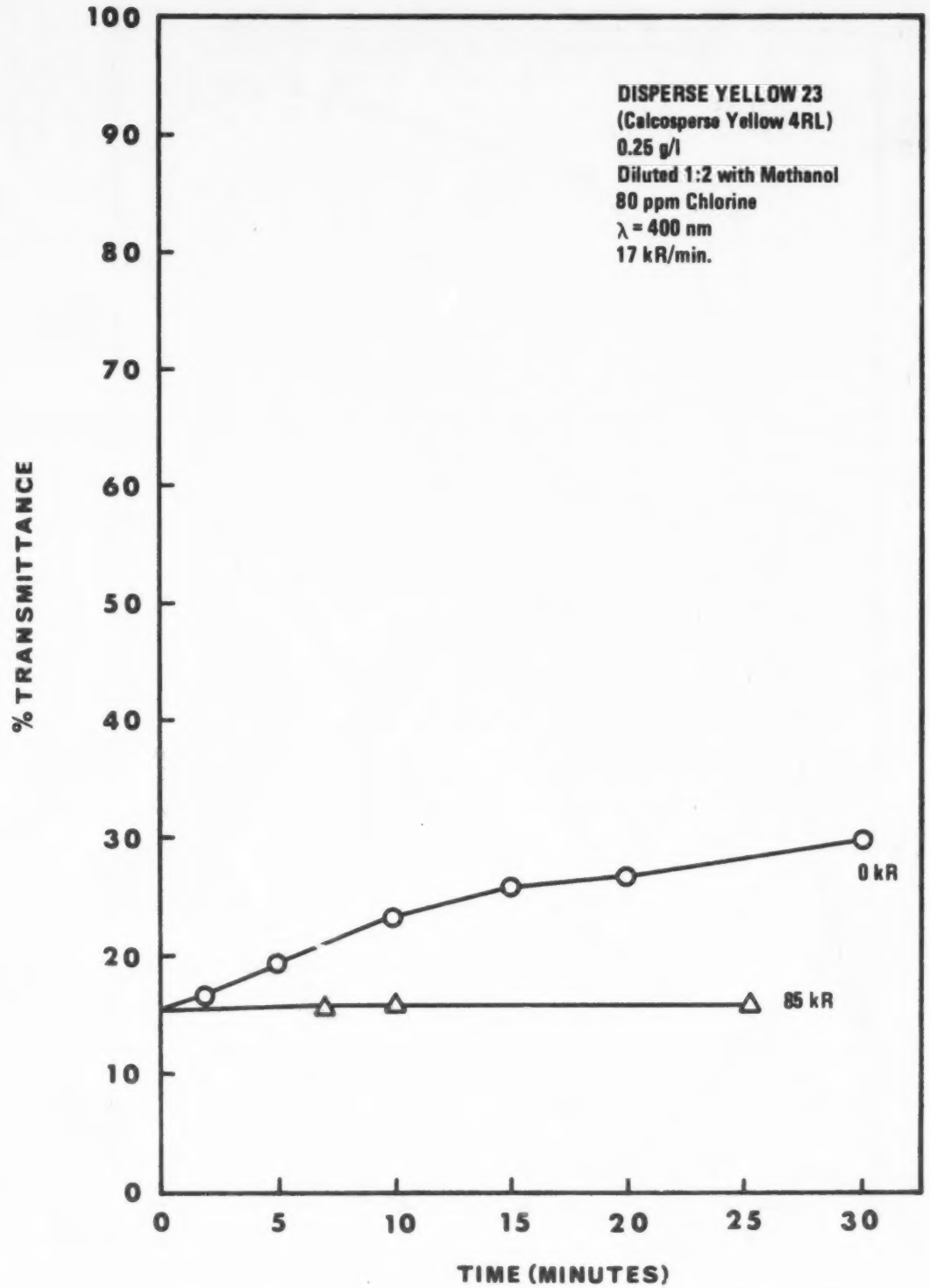

Figure 31 Transmittance Curves for Disperse Yellow 23

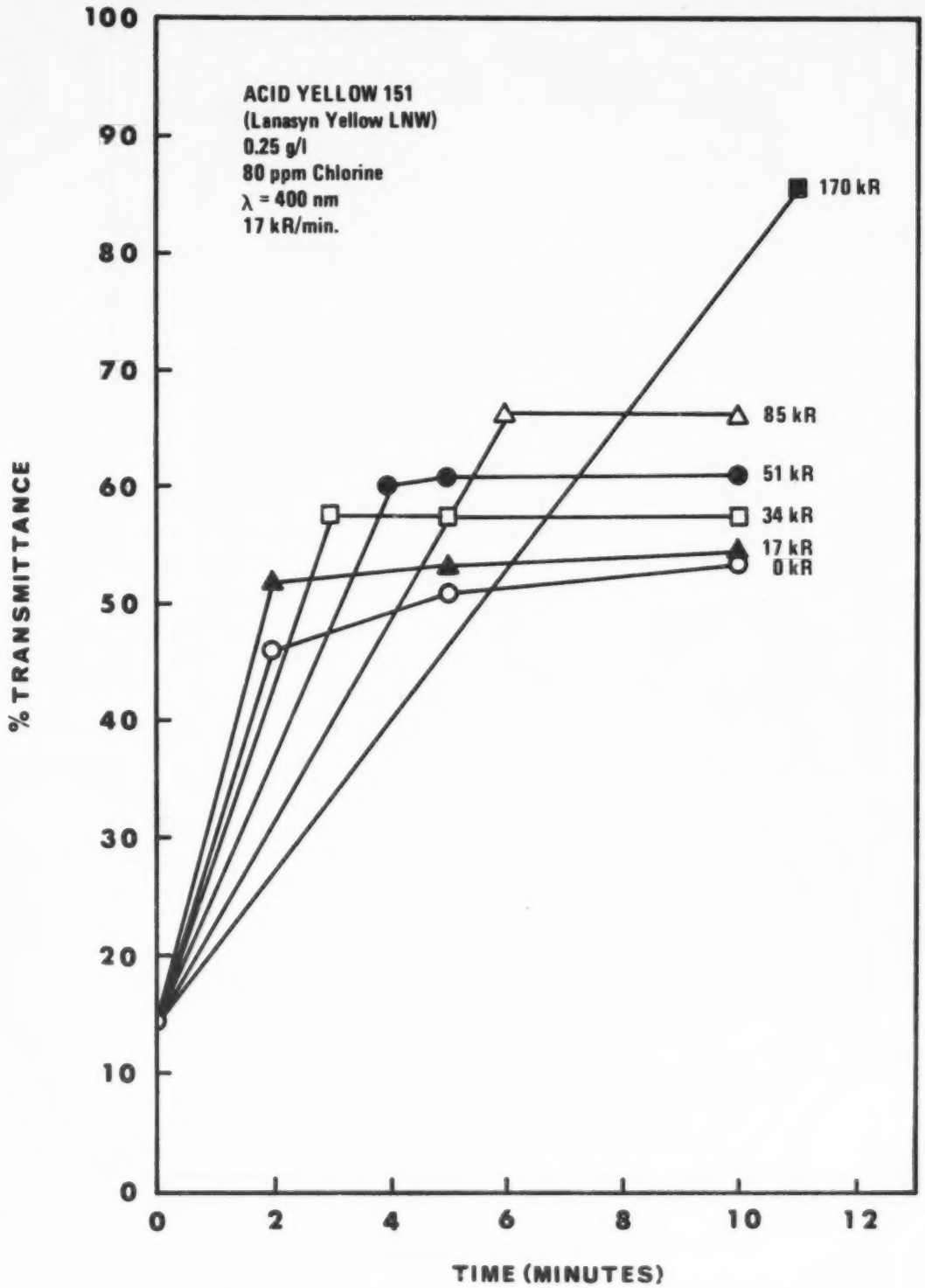

Figure 32 Transmittance Curves for Acid Yellow 151

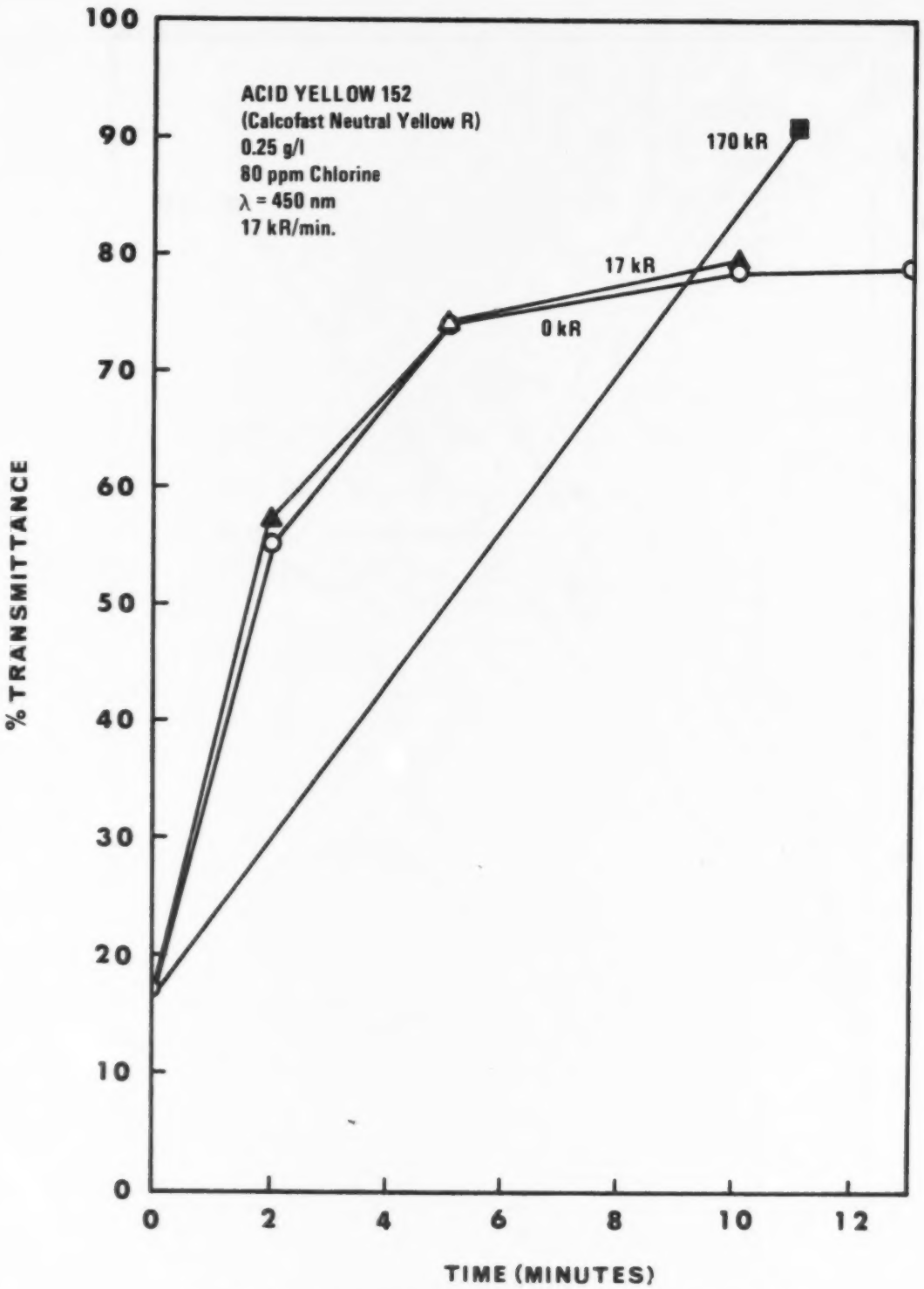

Figure 33 Transmittance Curves for Acid Yellow 152

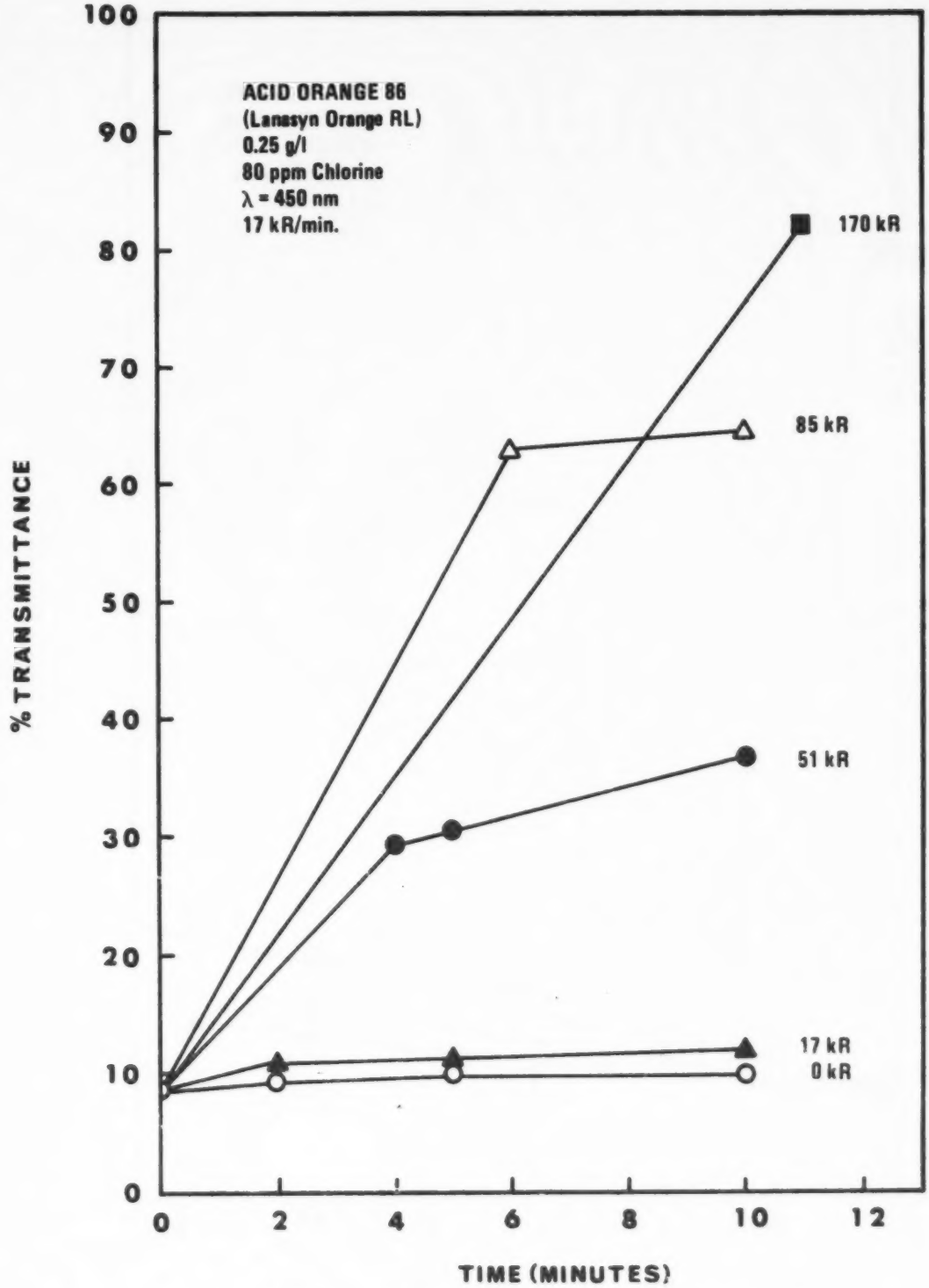

Figure 34 Transmittance Curves for Acid Orange 86 with 80 ppm Chlorine

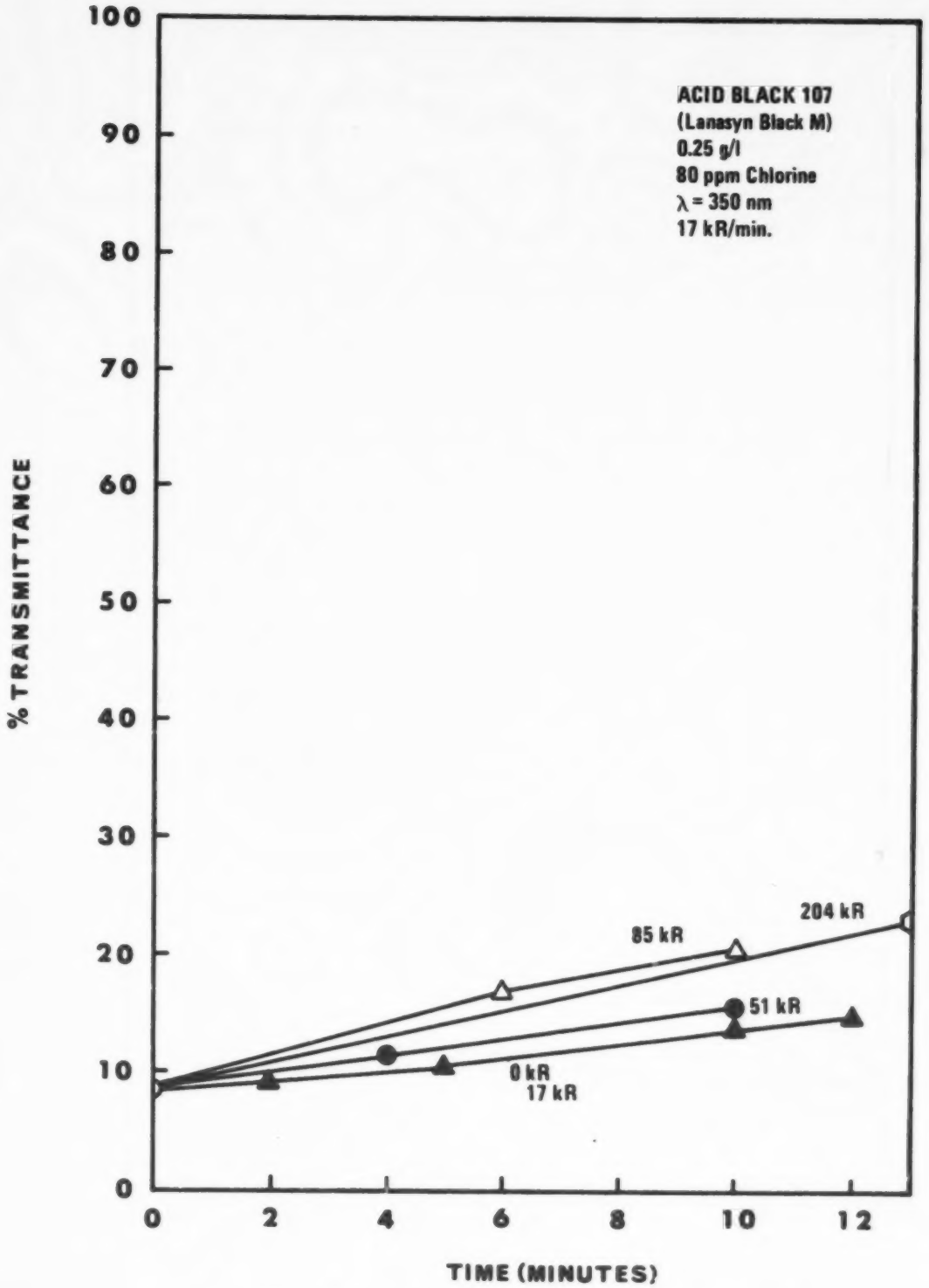

Figure 35 Transmittance Curves for Acid Black 107 with 80 ppm Chlorine

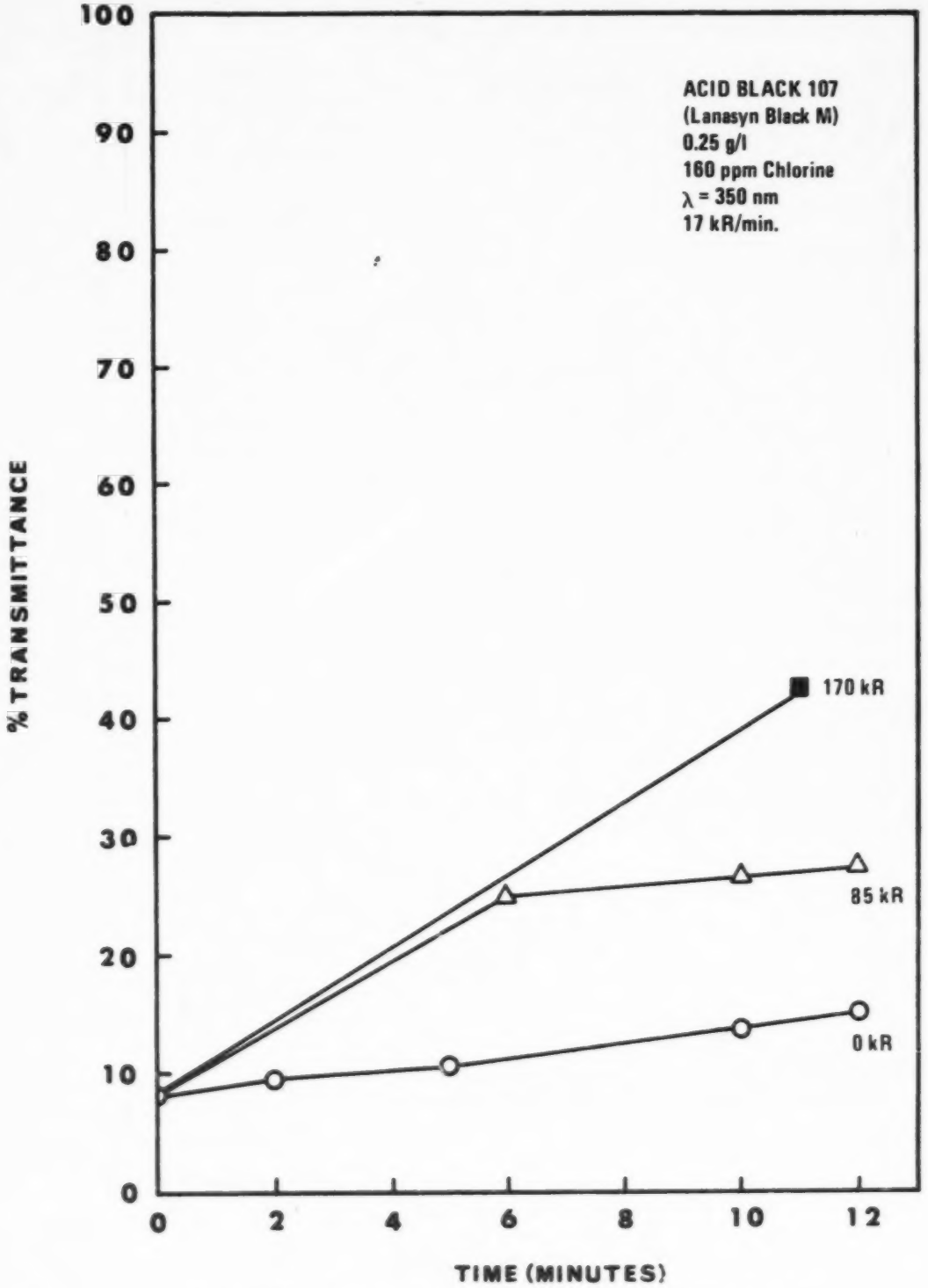

Figure 36 Transmittance Curves for Acid Black 107 with 160 ppm Chlorine

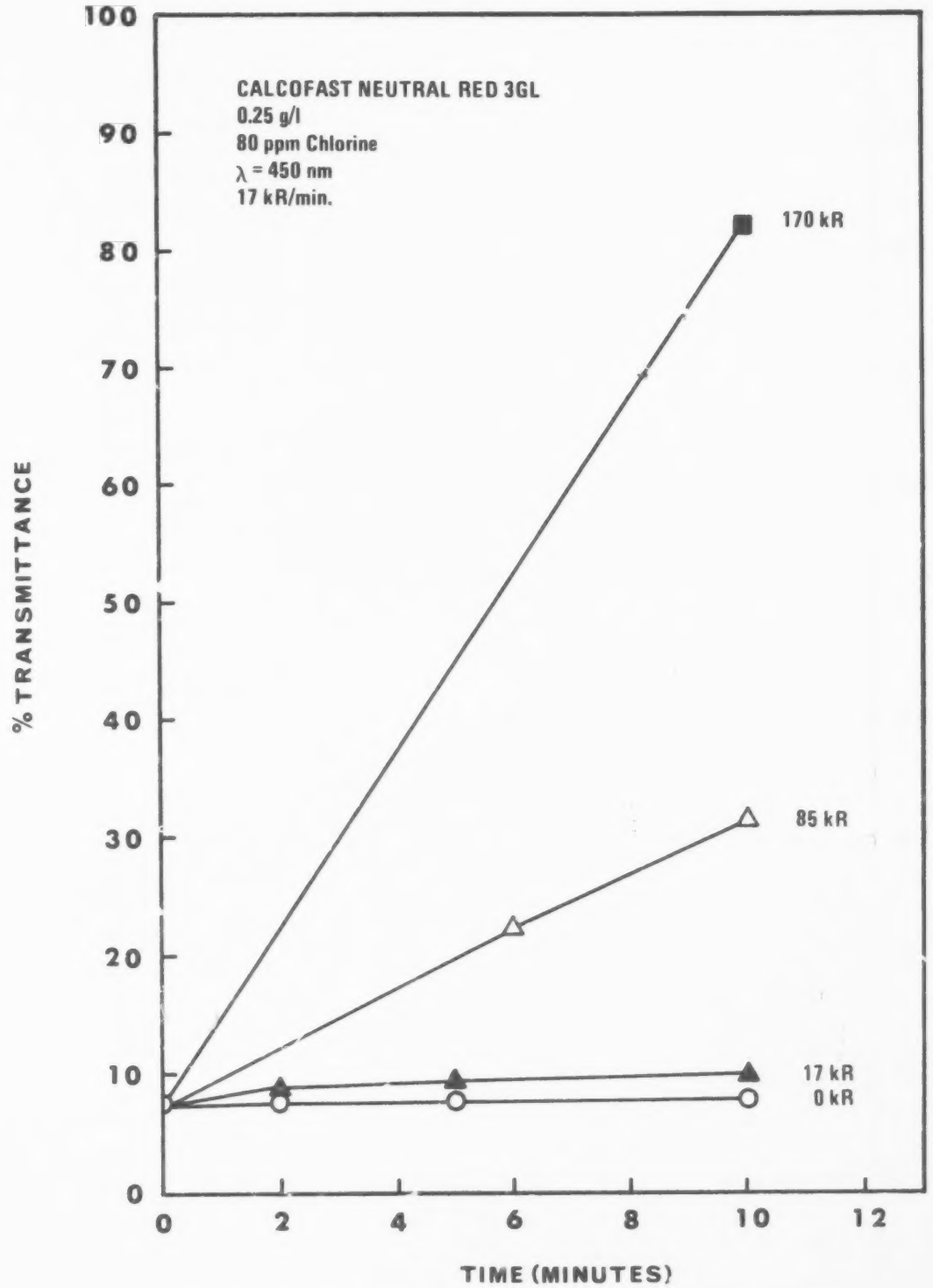

Figure 37 Transmittance Curves for Calcofast Neutral Red 3GL

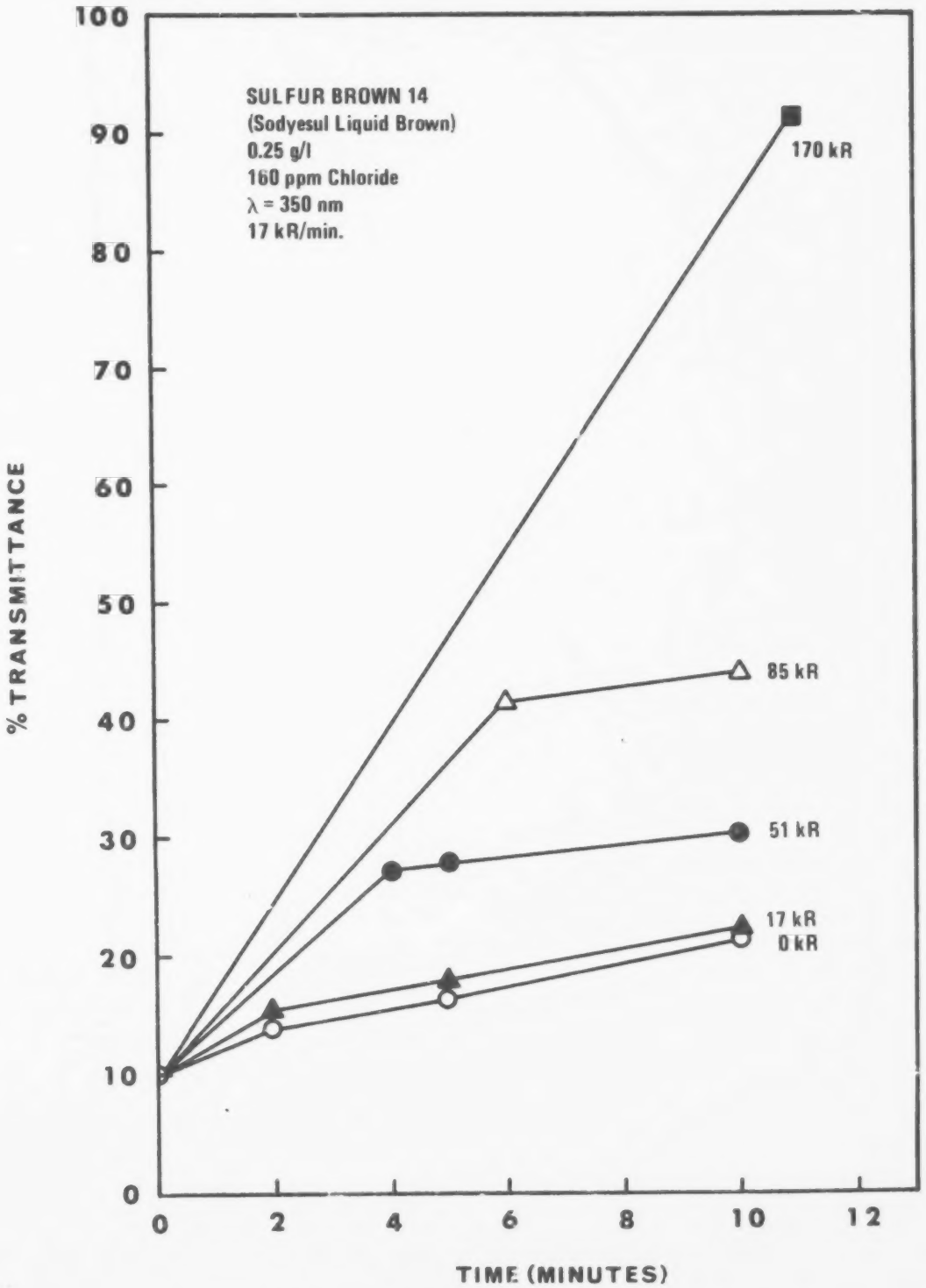

Figure 38 Transmittance Curves for Sulfur Brown 14

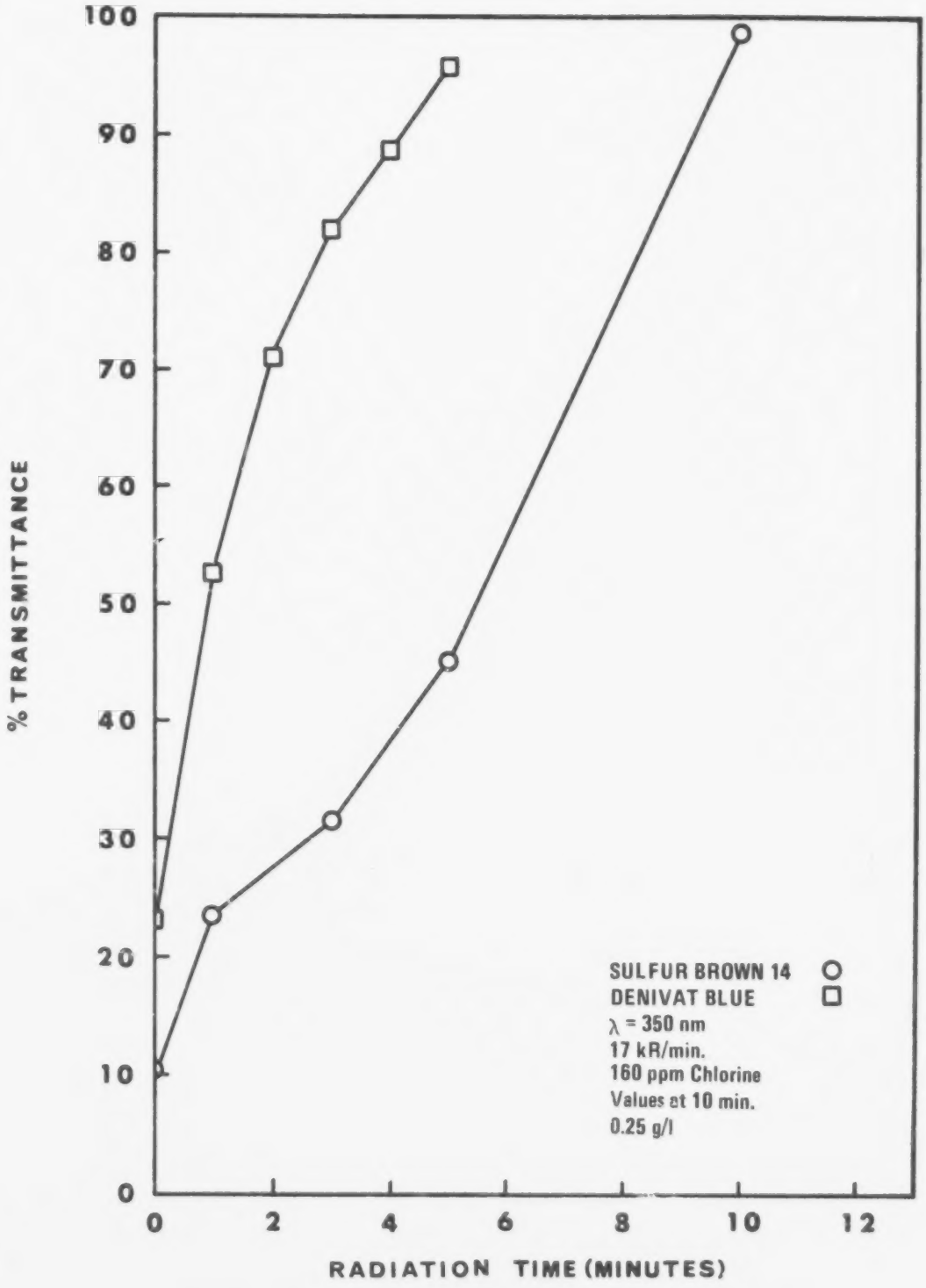

Figure 39 Transmittance Curves for Sulfur Brown 14 and Denivat Blue 57

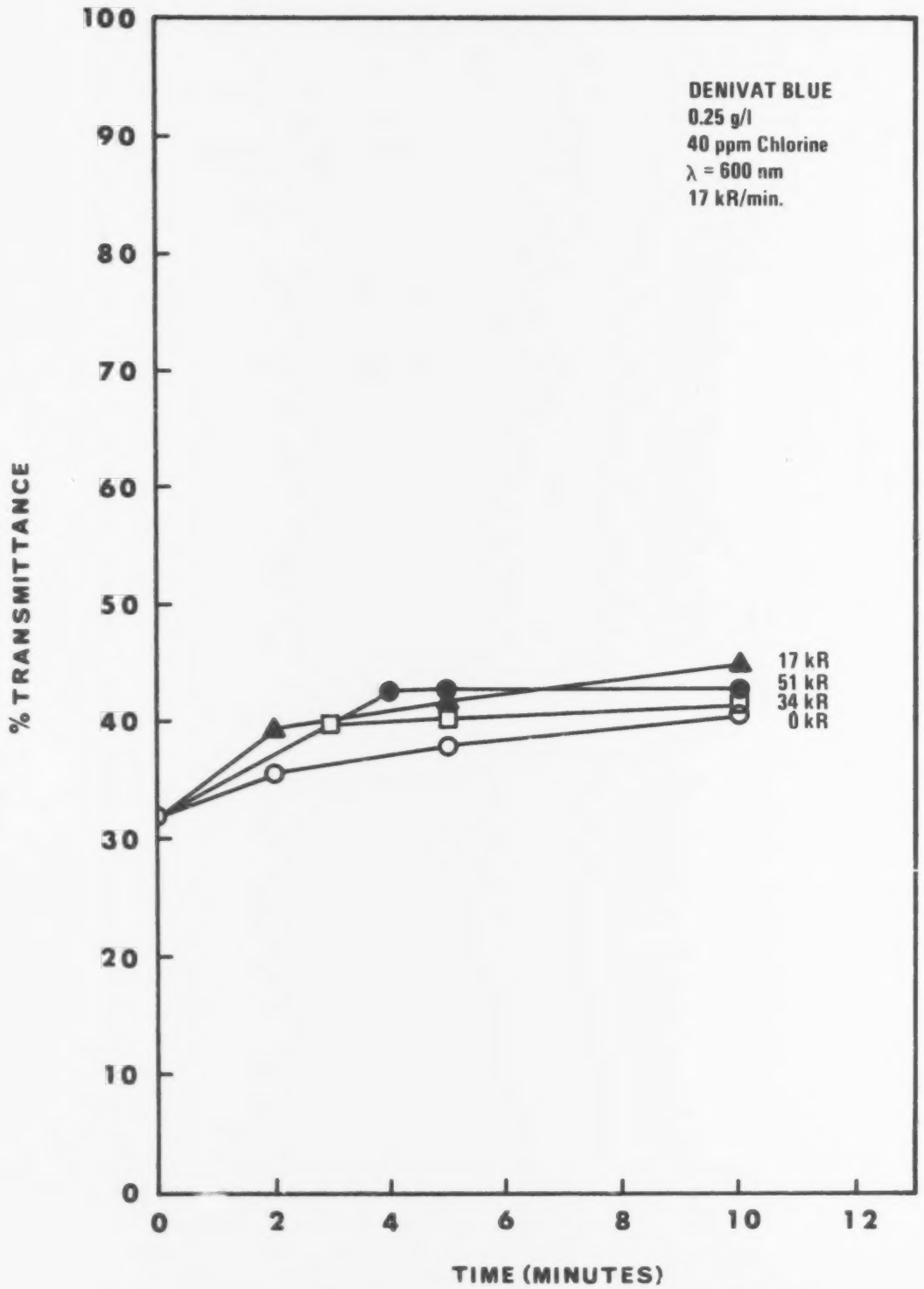

Figure 40 Transmittance Curves for Denivat Blue 57 with 40 ppm Chlorine

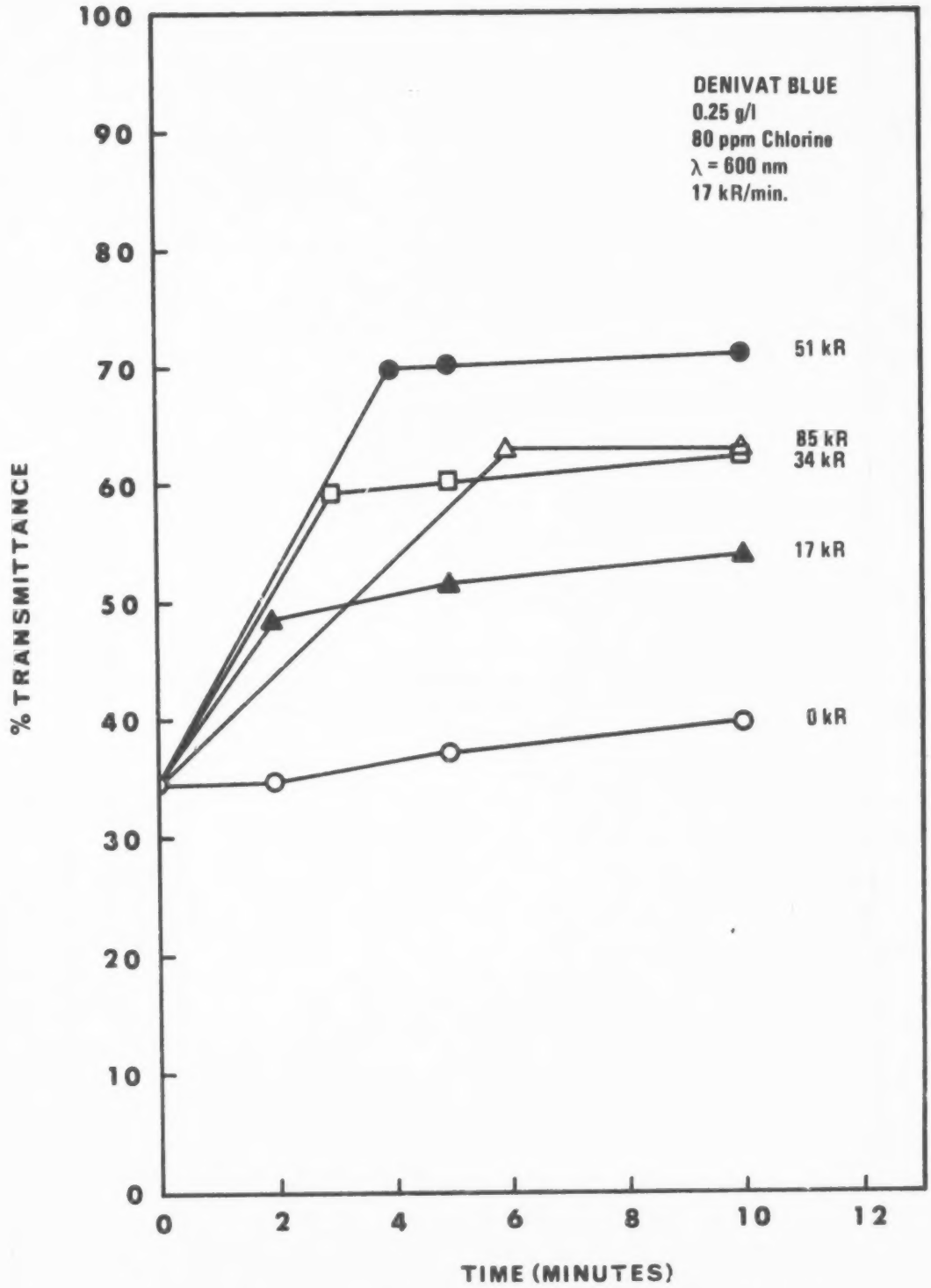

Figure 41 Transmittance Curves for Denivat Blue 57 with 80 ppm Chlorine

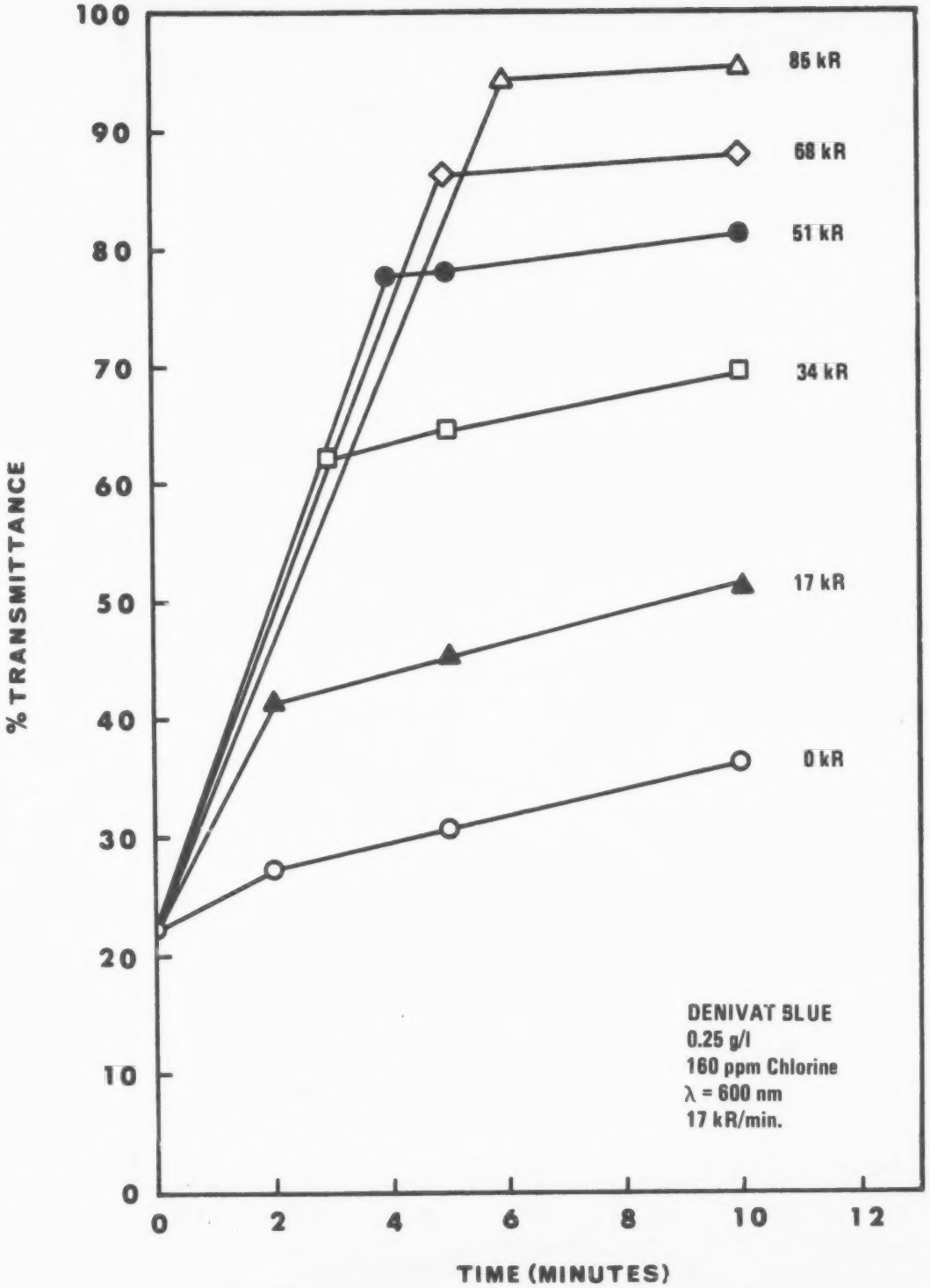

Figure 42 Transmittance Curves for Denivat Blue 57 with 160 ppm Chlorine

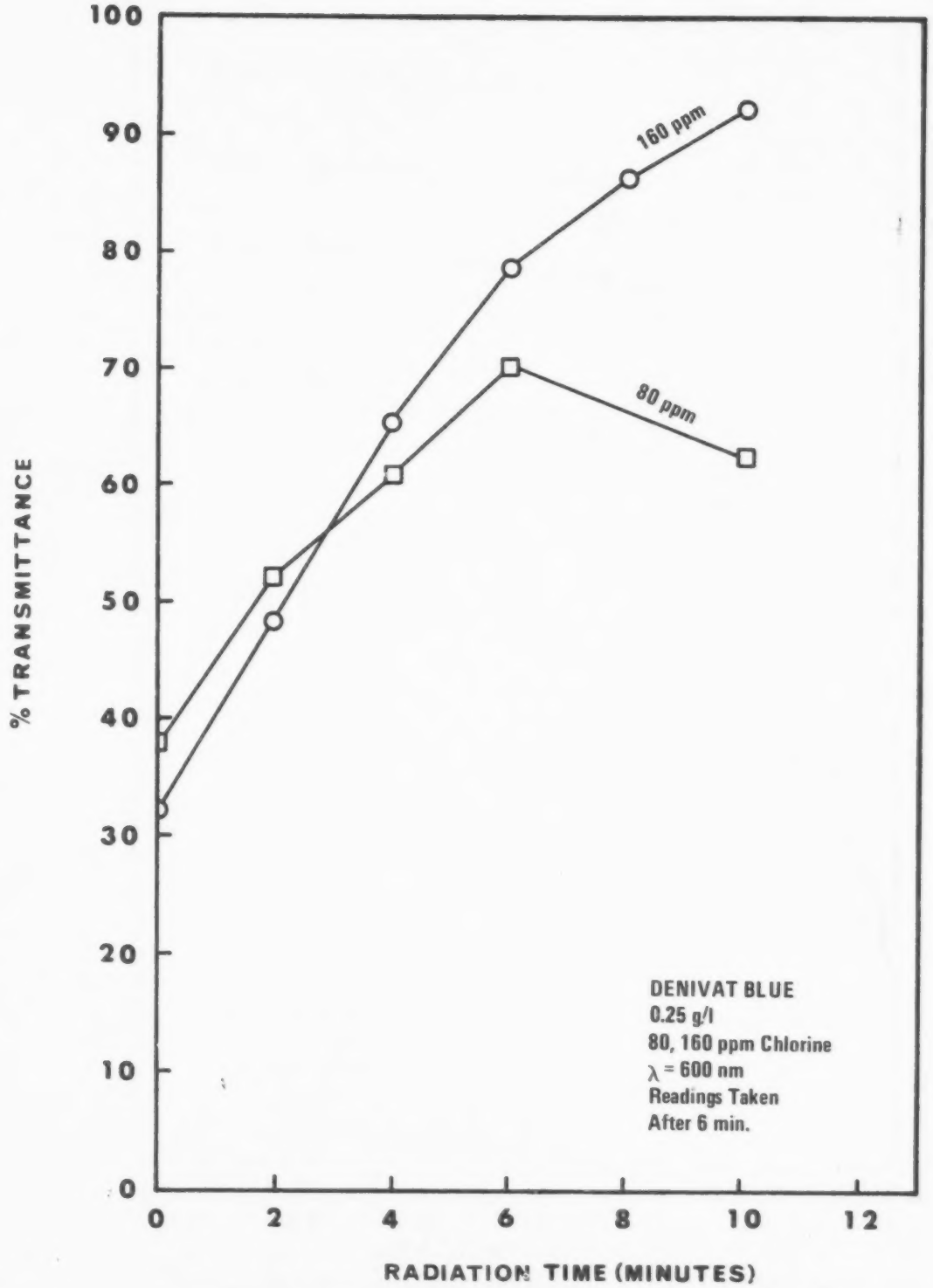

Figure 43 Transmittance Curves for Denivat Blue 57 for Various Radiation Doses

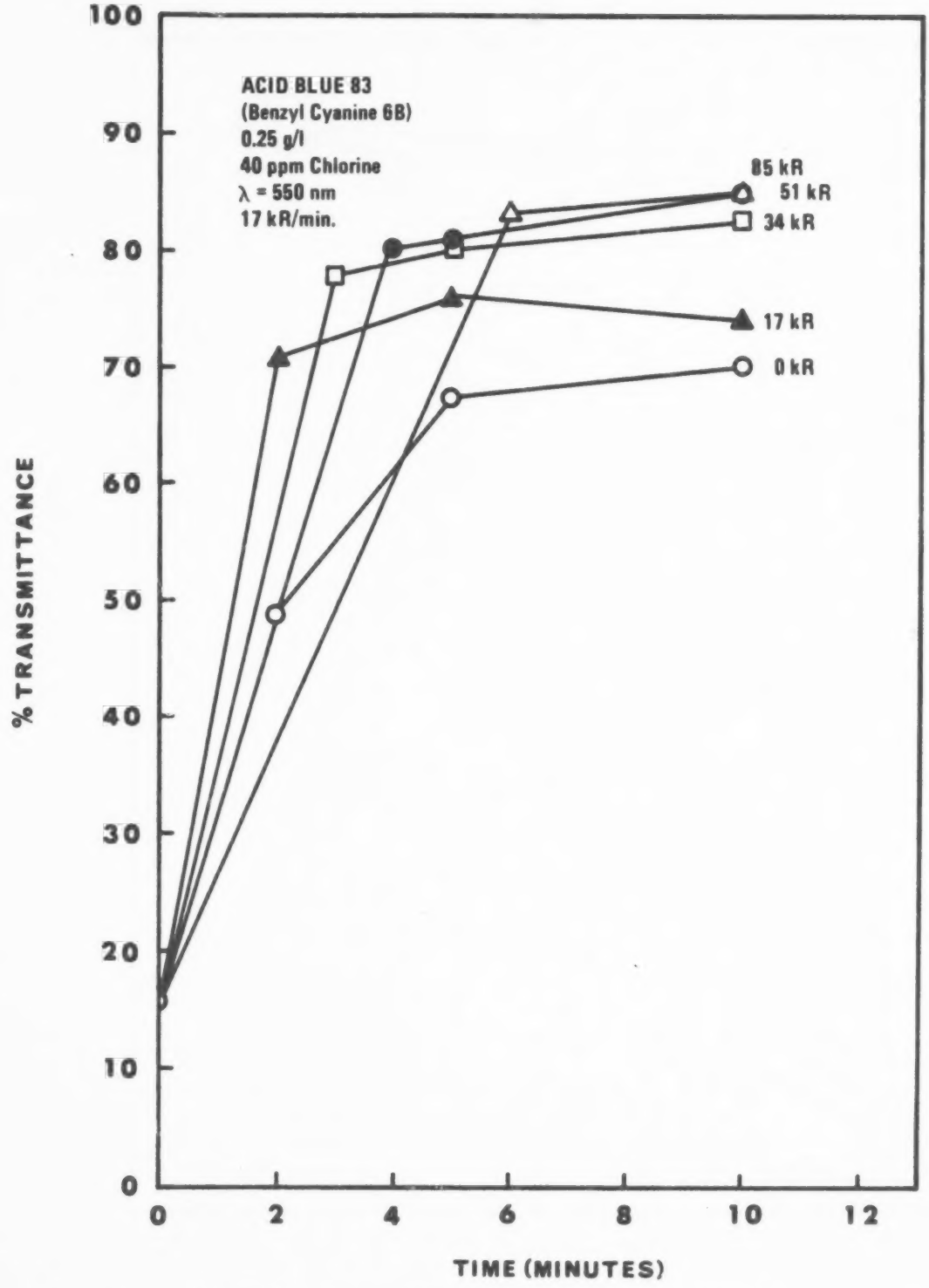

Figure 44 Transmittance Curves for Acid Blue 83 with 40 ppm Chlorine

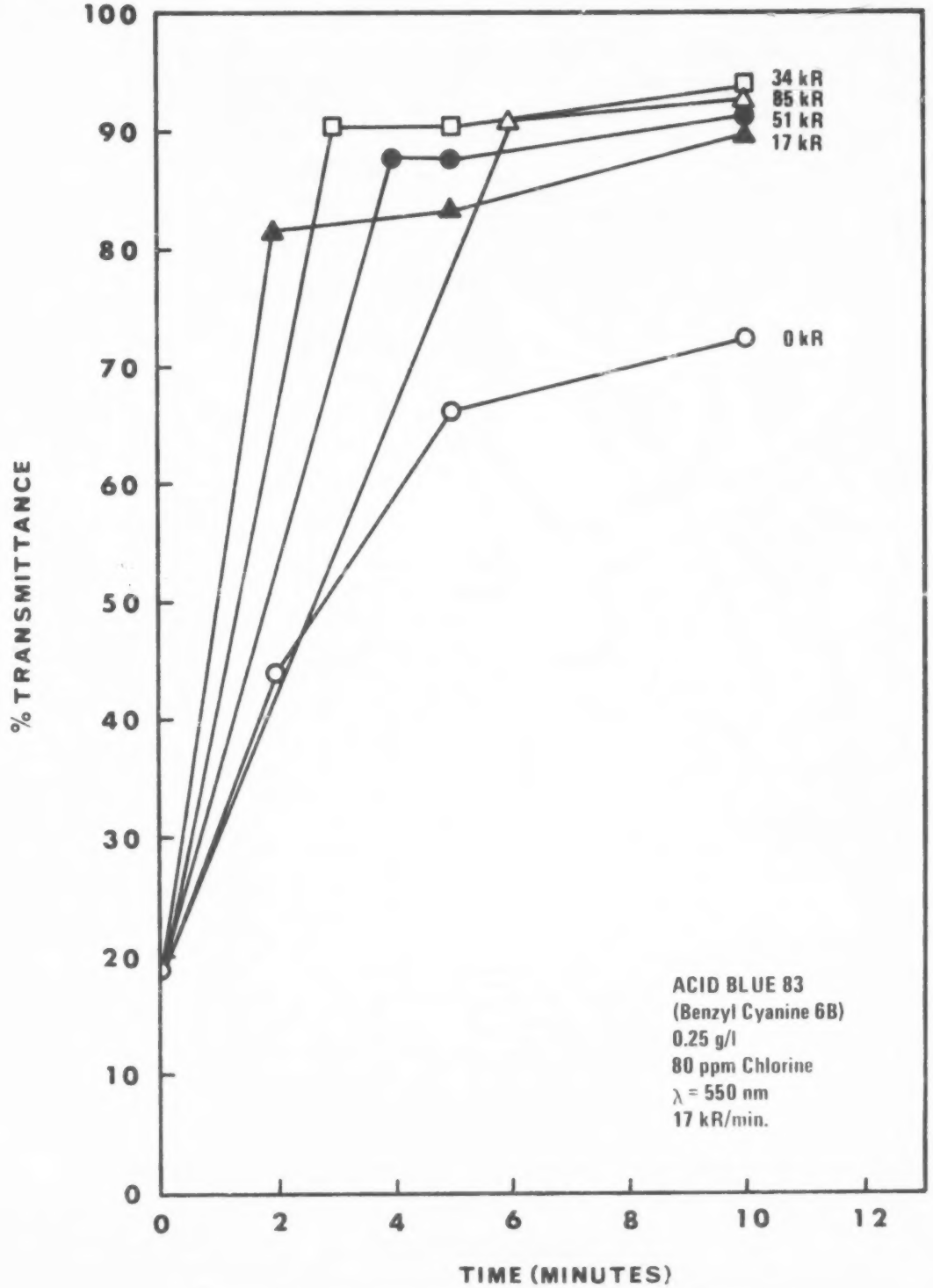

Figure 45 Transmittance Curves for Acid Blue 83 with 80 ppm Chlorine

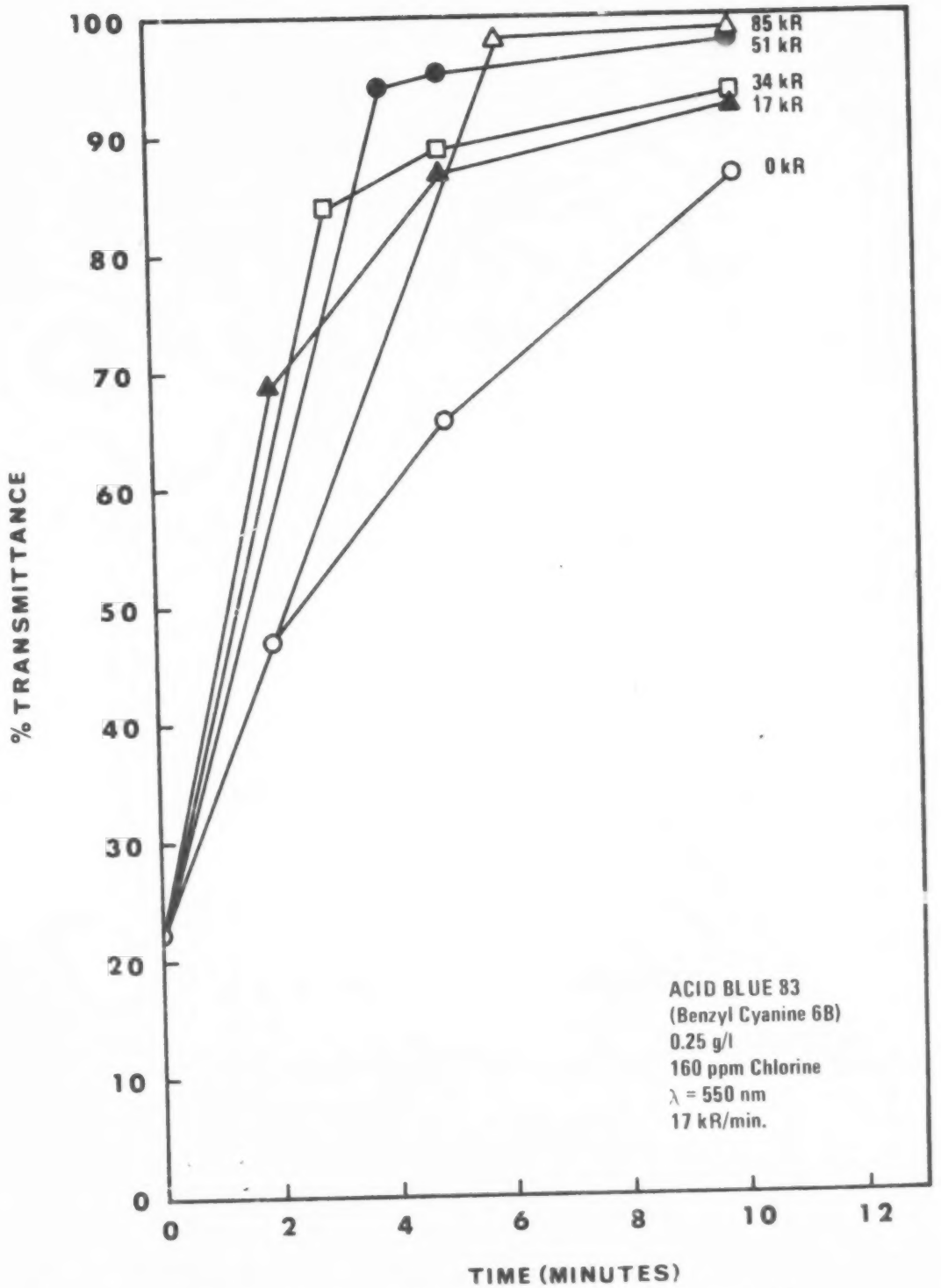

Figure 46 Transmittance Curves for Acid Blue 83 with 160 ppm Chlorine

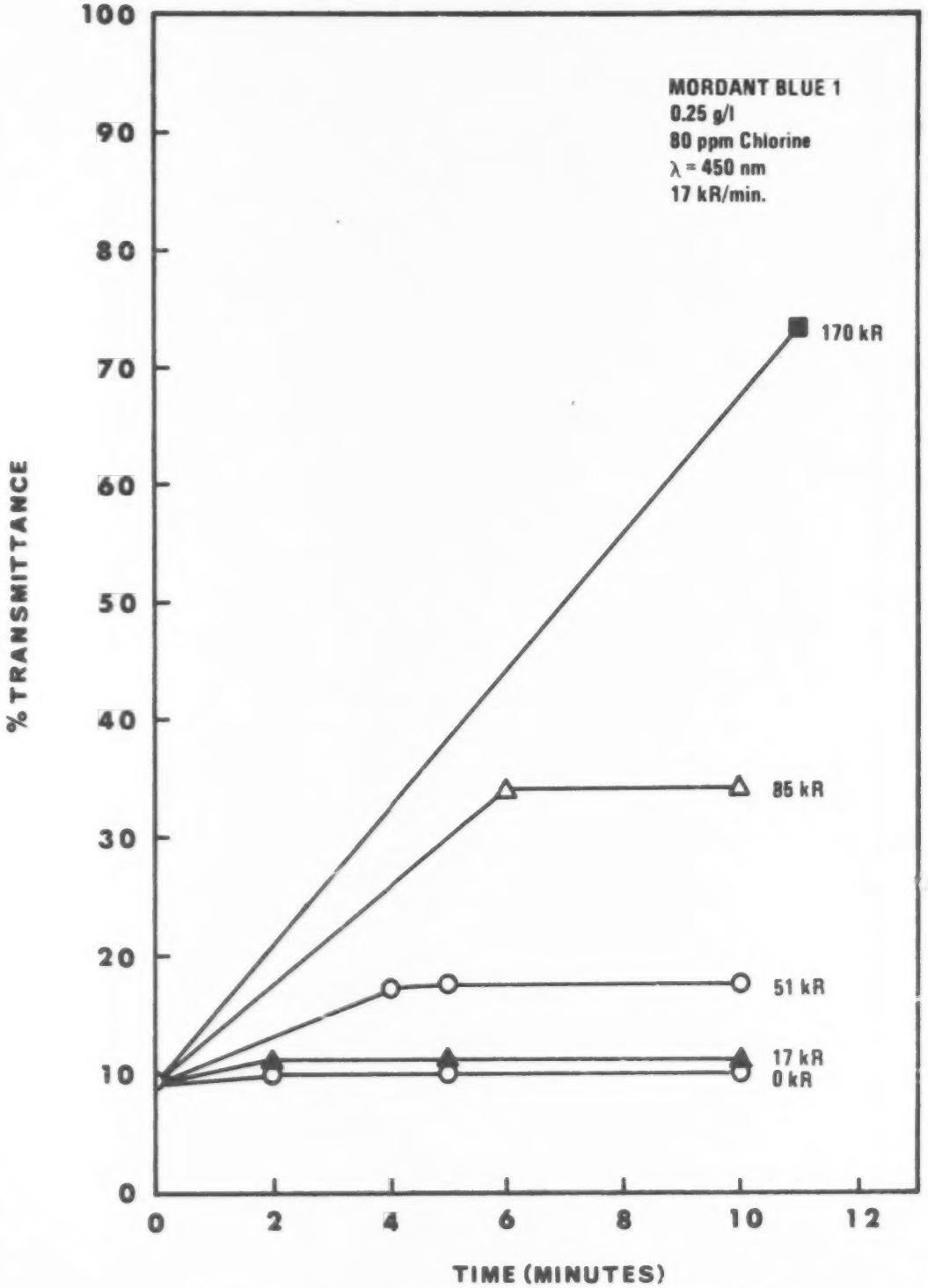

Figure 47 Transmittance Curves for Mordant Blue 1 with 80 ppm Chlorine

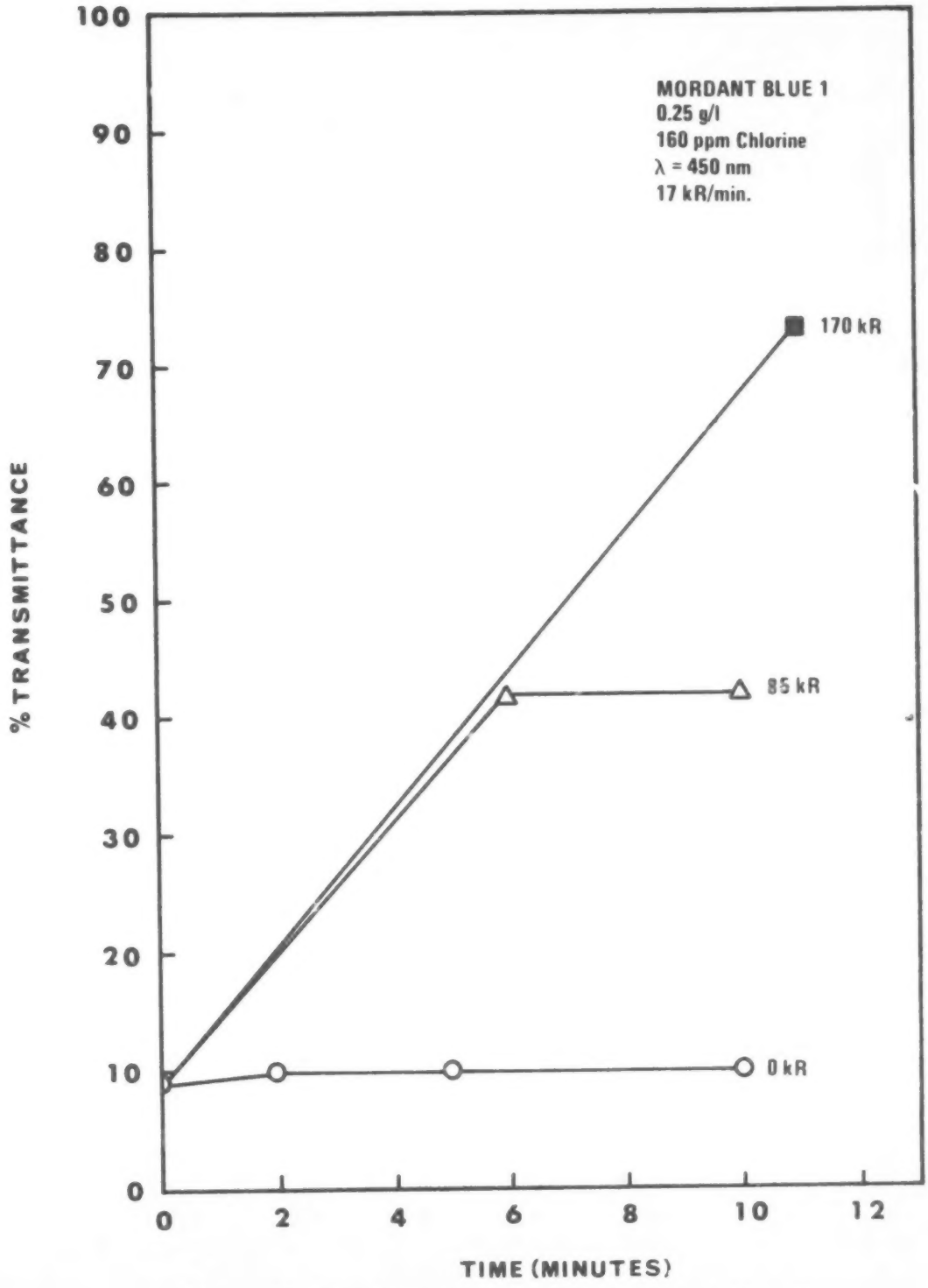

Figure 48 Transmittance Curves for Mordant Blue 1 with 160 ppm Chlorine

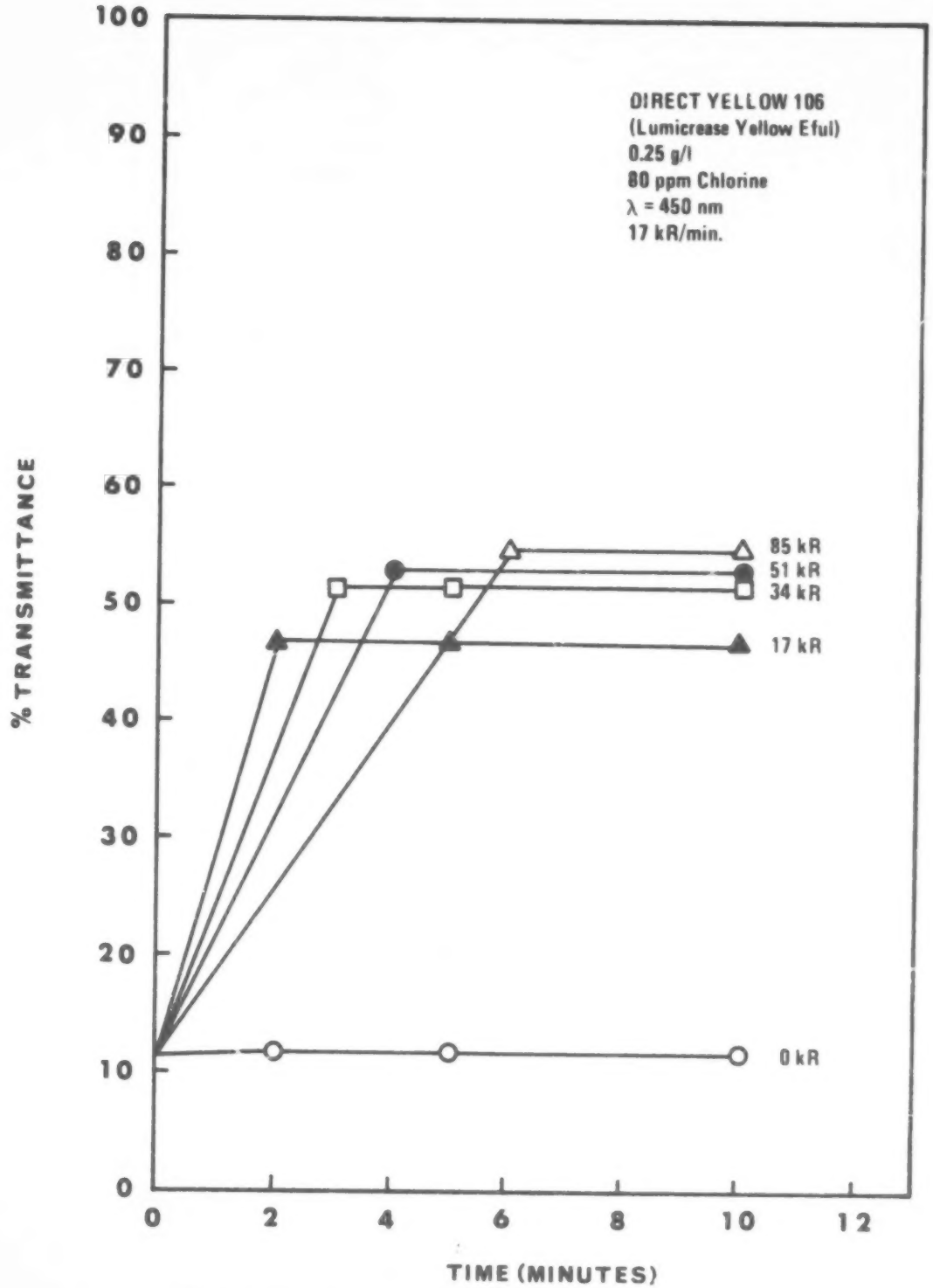

Figure 49 Transmittance Curves for Direct Yellow 106 with 80 ppm Chlorine

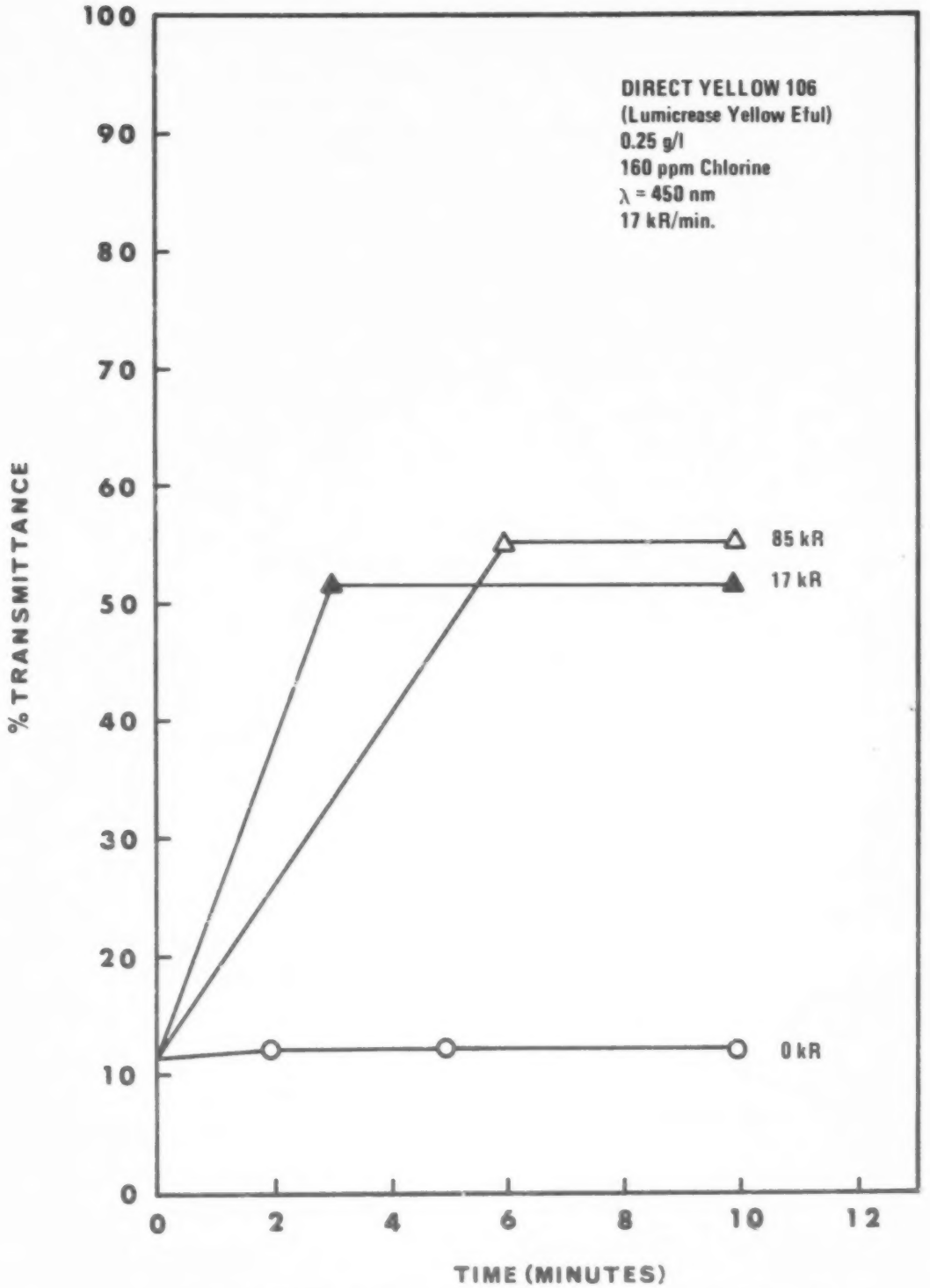

Figure 50 Transmittance Curves for Direct Yellow 106 with 160 ppm Chlorine

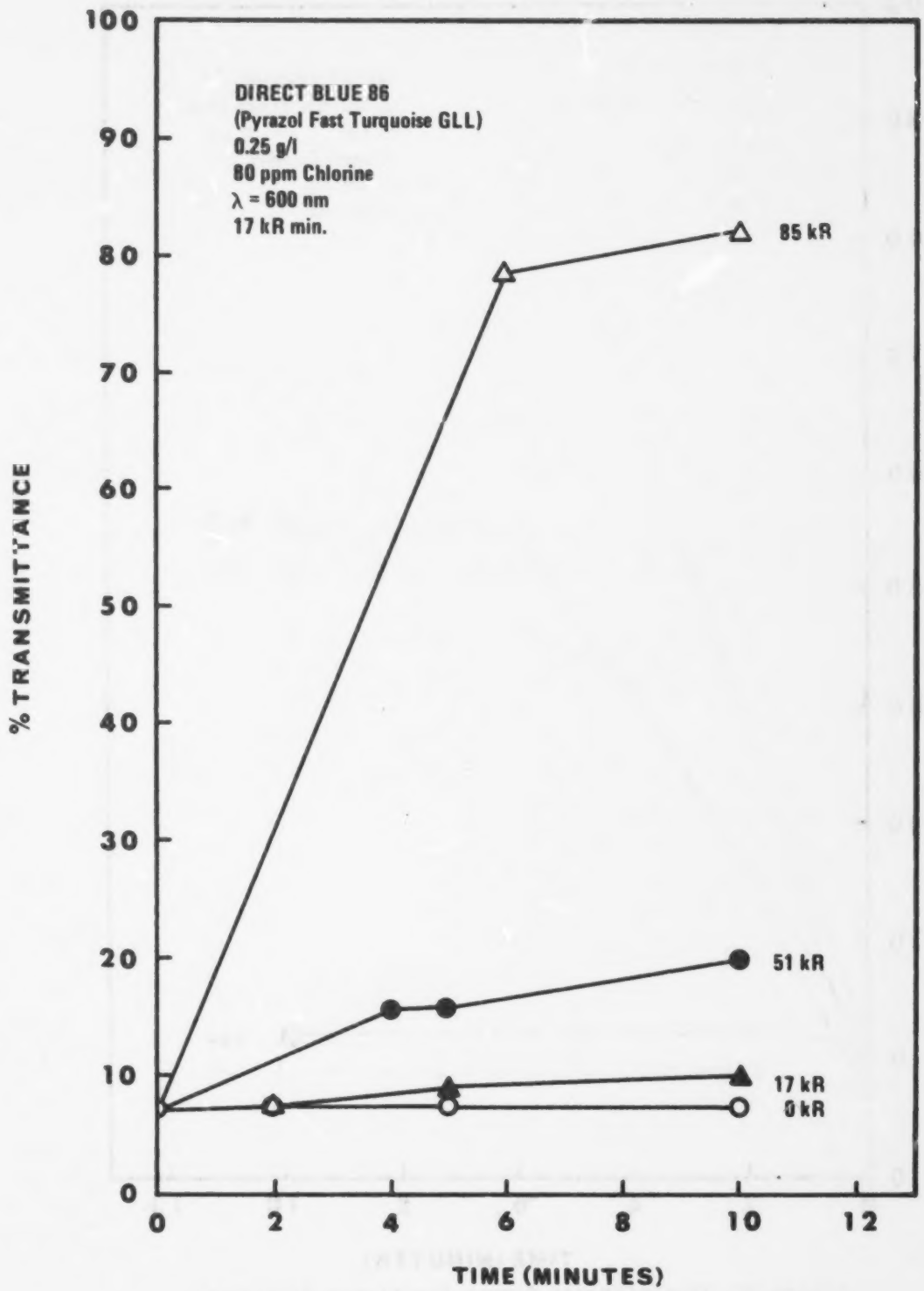

Figure 51 Transmittance Curves for Direct Blue 86 with 80 ppm Chlorine

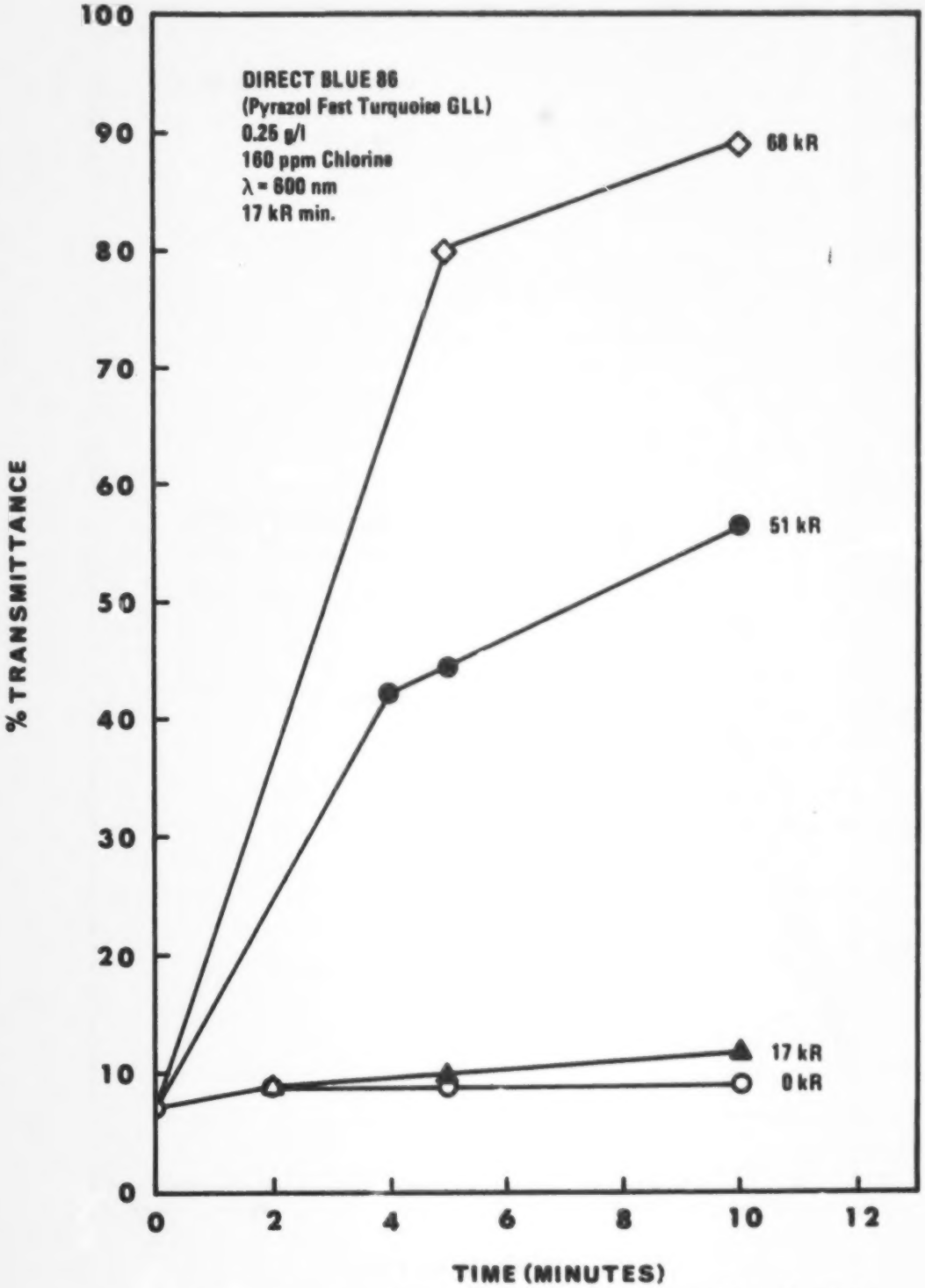

Figure 52 Transmittance Curves for Direct Blue 86 with 160 ppm Chlorine

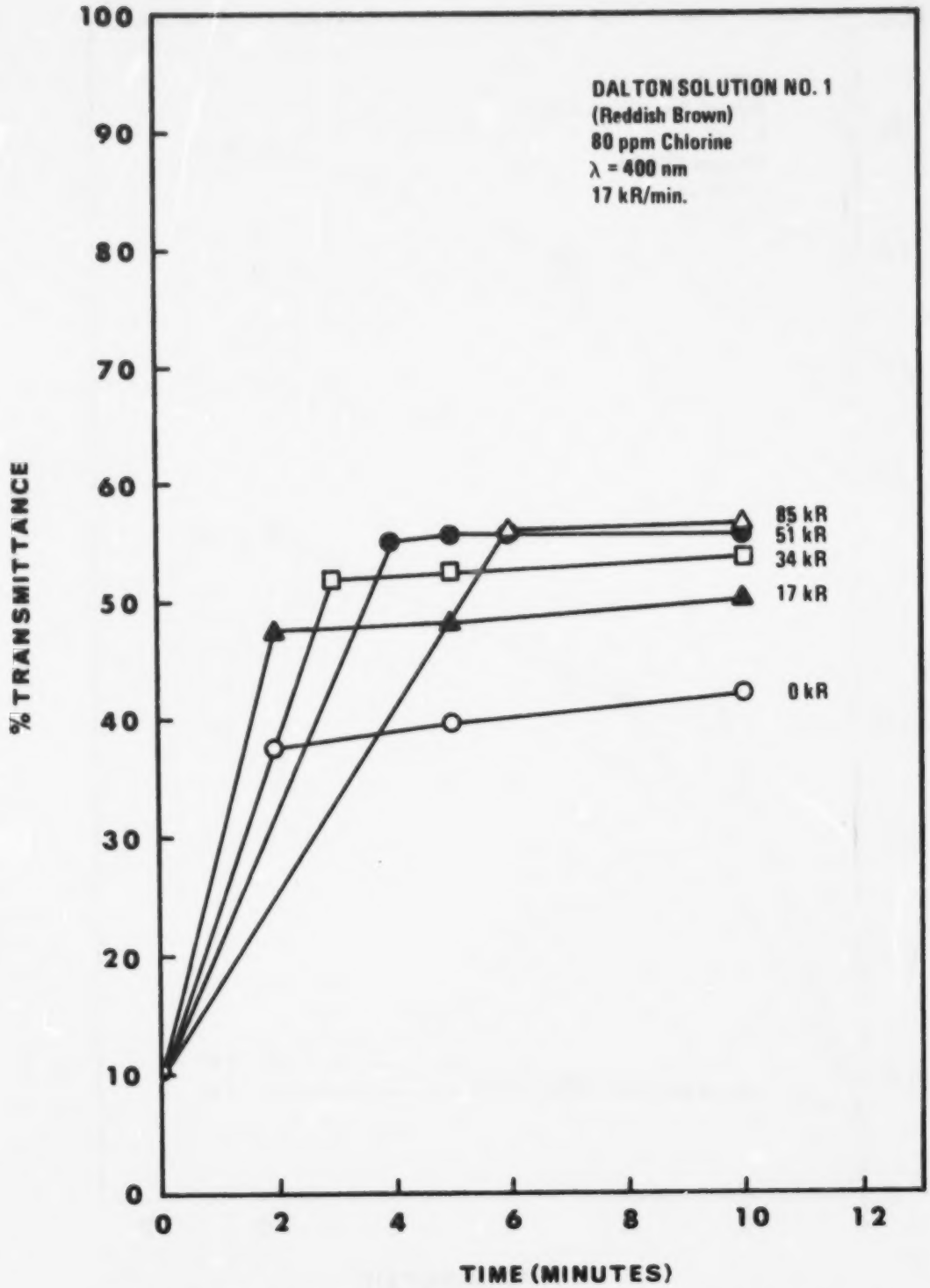

Figure 53 Transmittance Curves for Dalton Solution No. 1

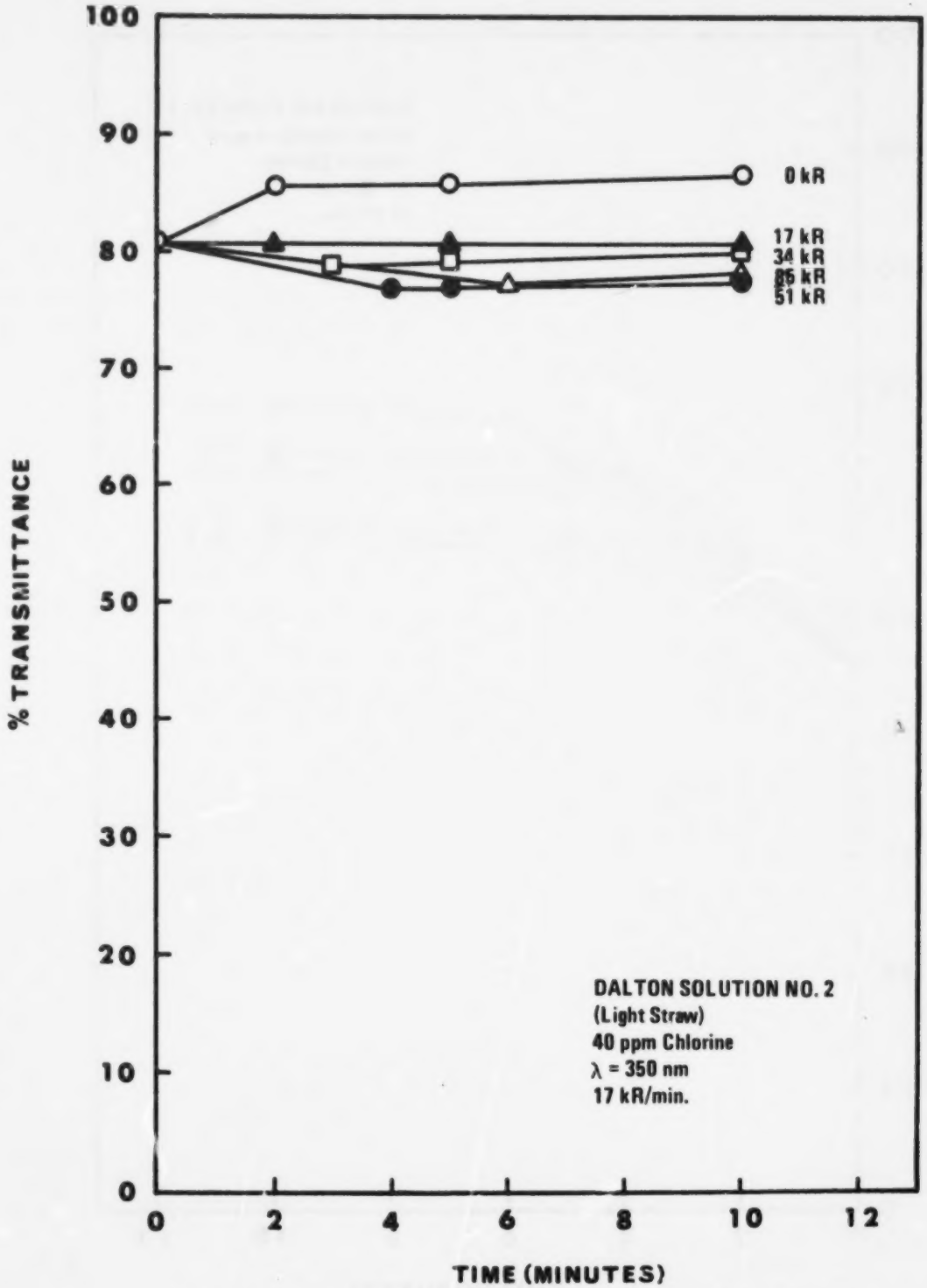

Figure 54 Transmittance Curves for Dalton Solution No. 2

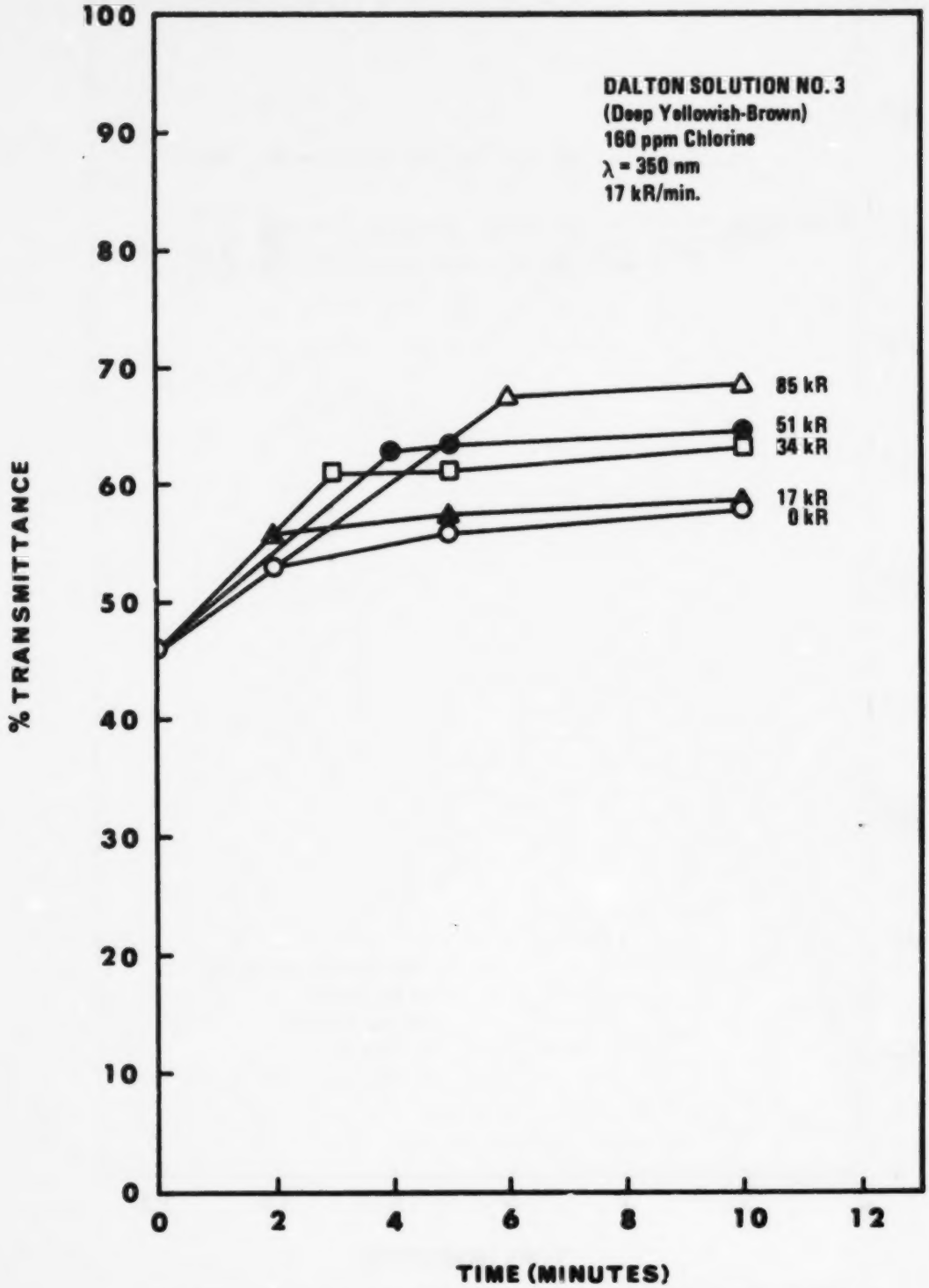

Figure 55 Transmittance Curves for Dalton Solution No. 3

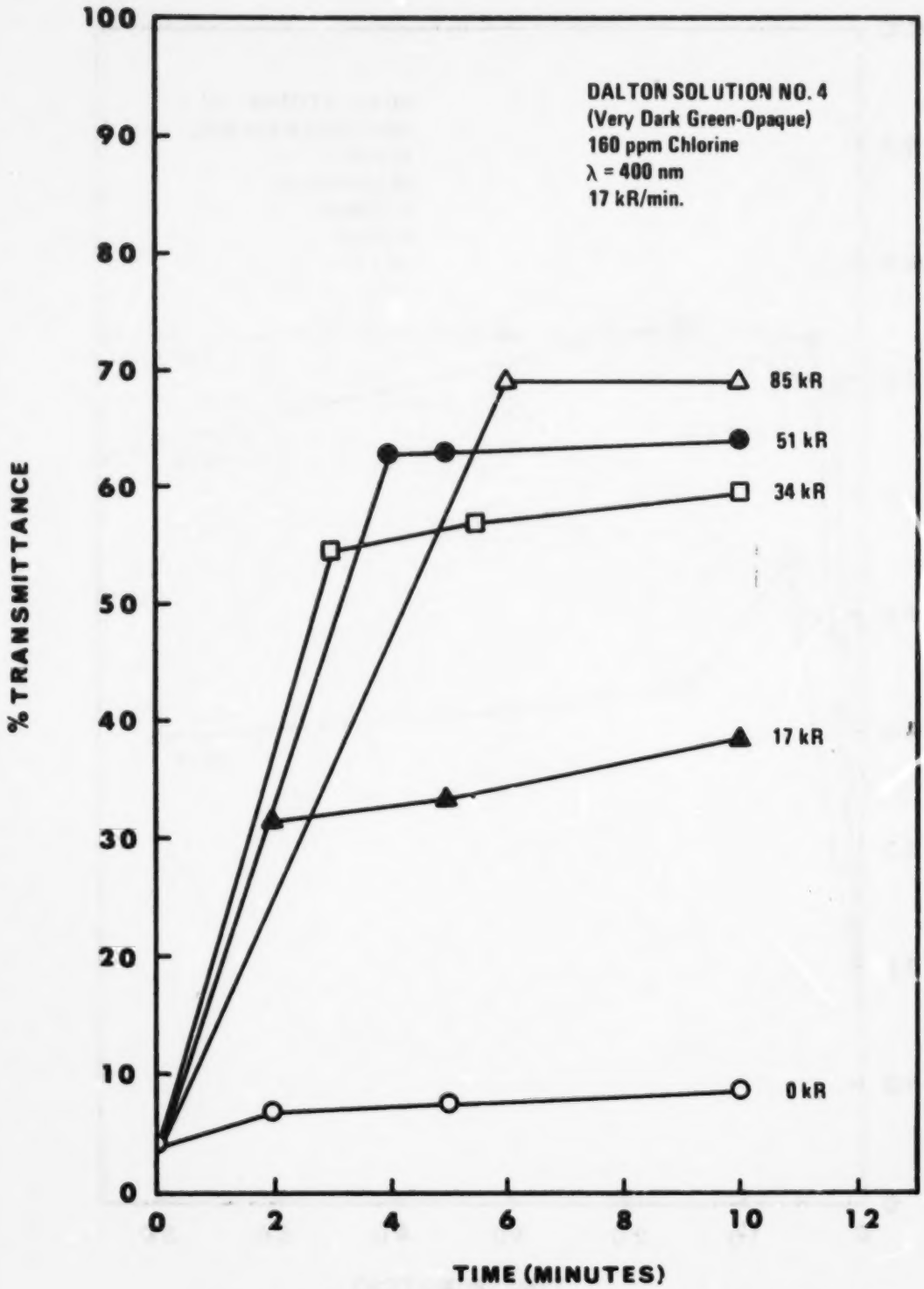

Figure 56 Transmittance Curves for Dalton Solution No. 4

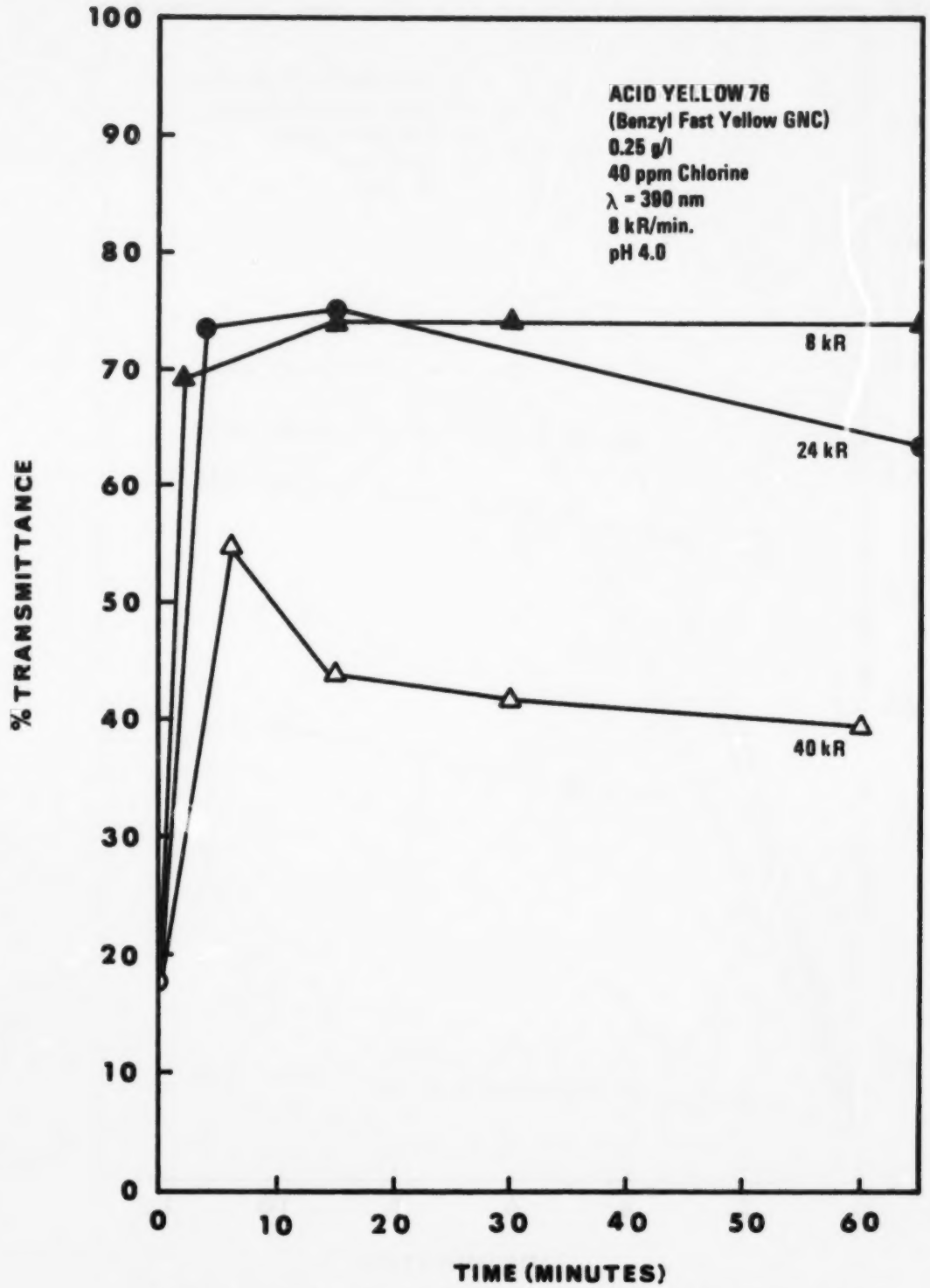

Figure 57 Transmittance Curves for Acid Yellow 76 at pH 4.0

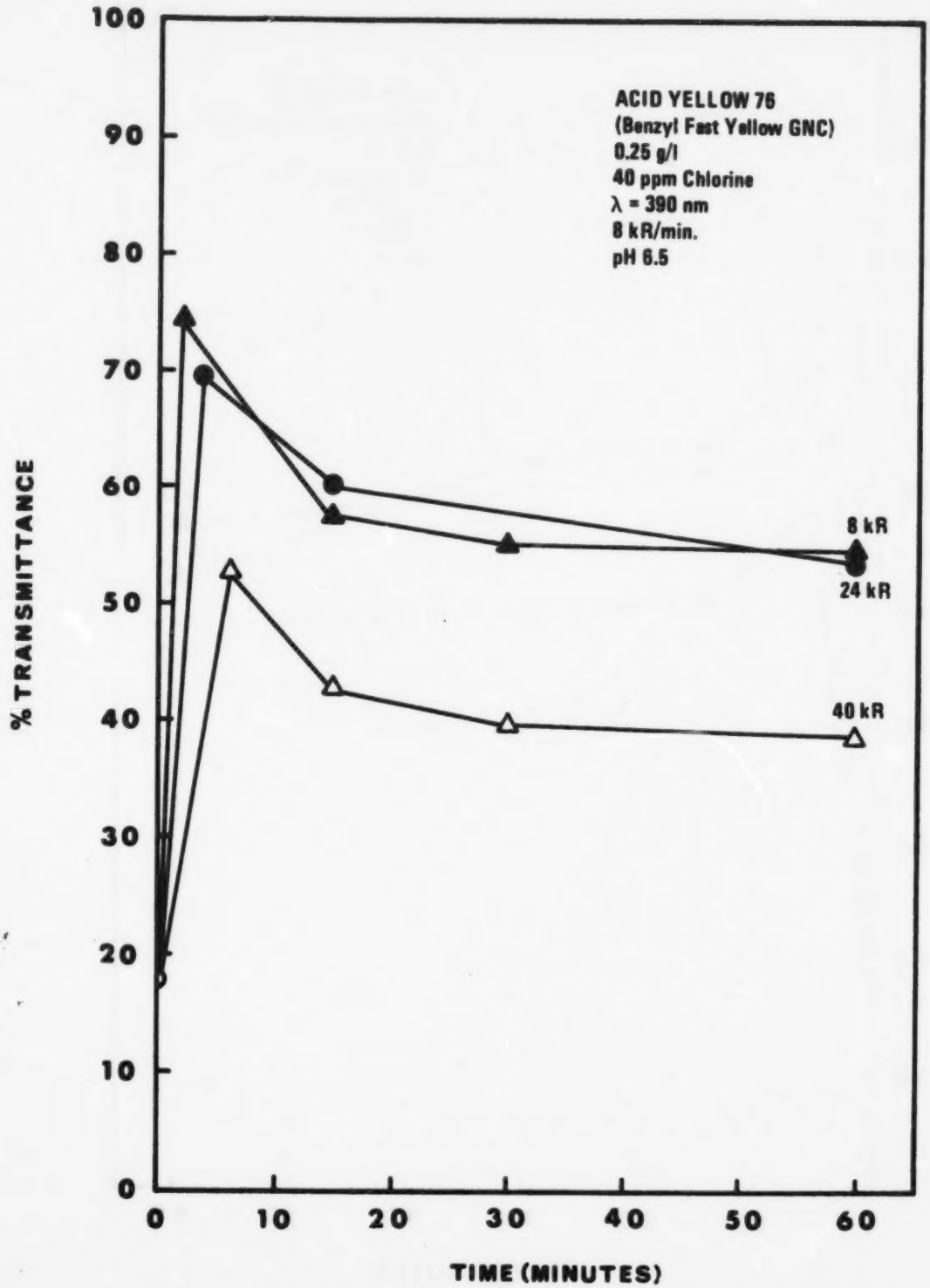

Figure 58 Transmittance Curves for Acid Yellow 76 at pH 6.5

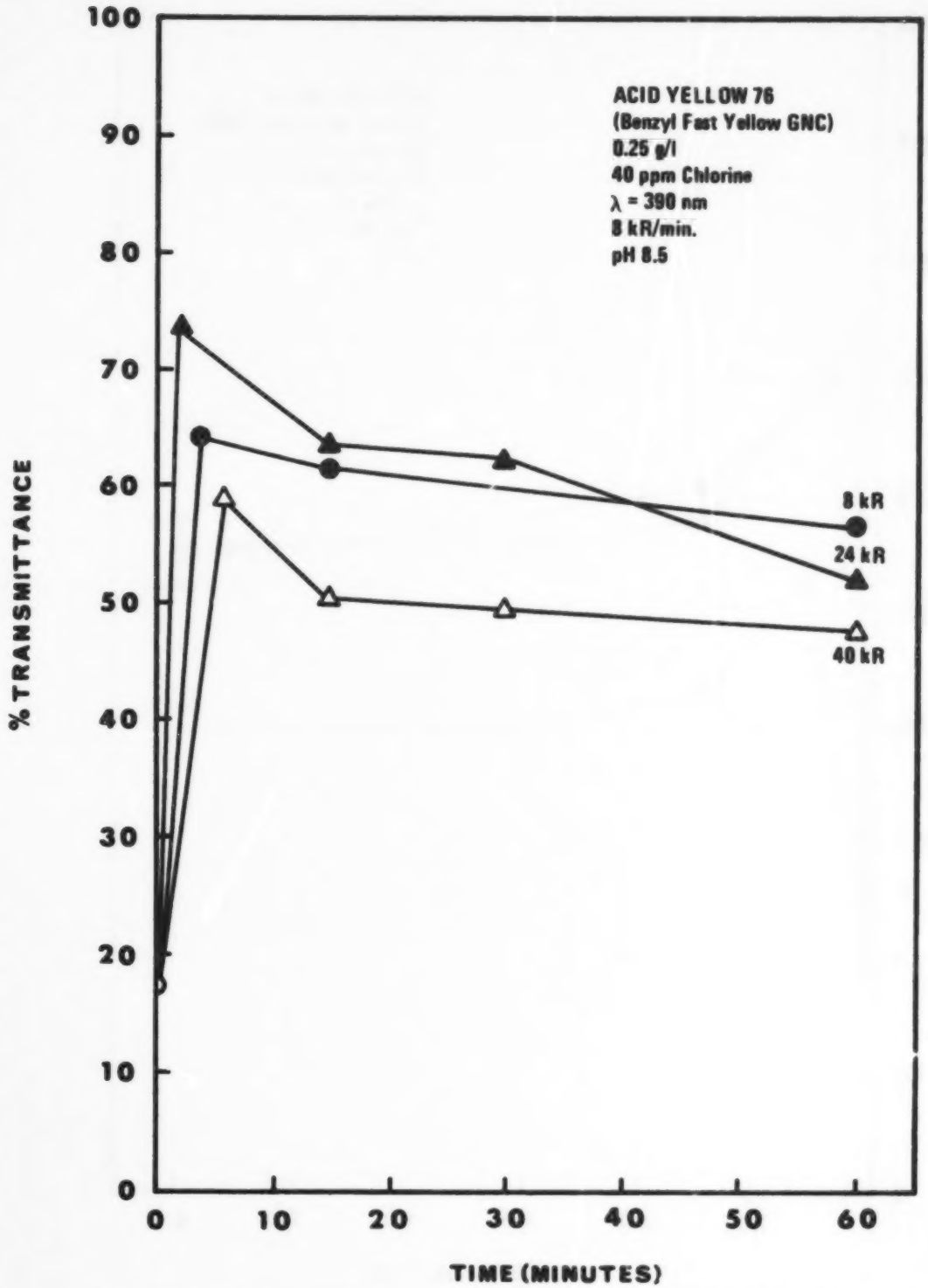

Figure 59 Transmittance Curves for Acid Yellow 76 at pH 8.5

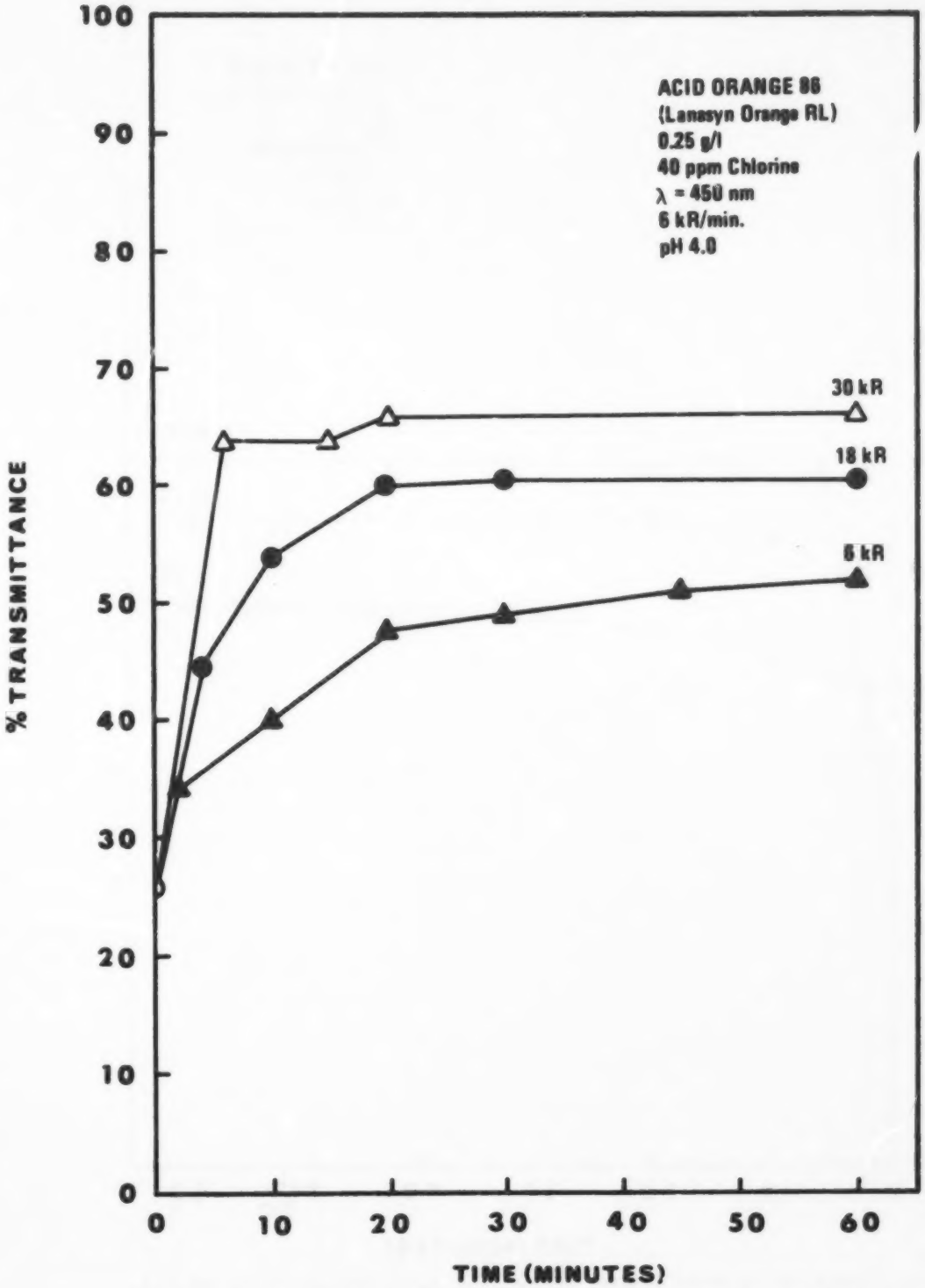

Figure 60 Transmittance Curves for Acid Orange 86 at pH 4.0 with 40 ppm Chlorine

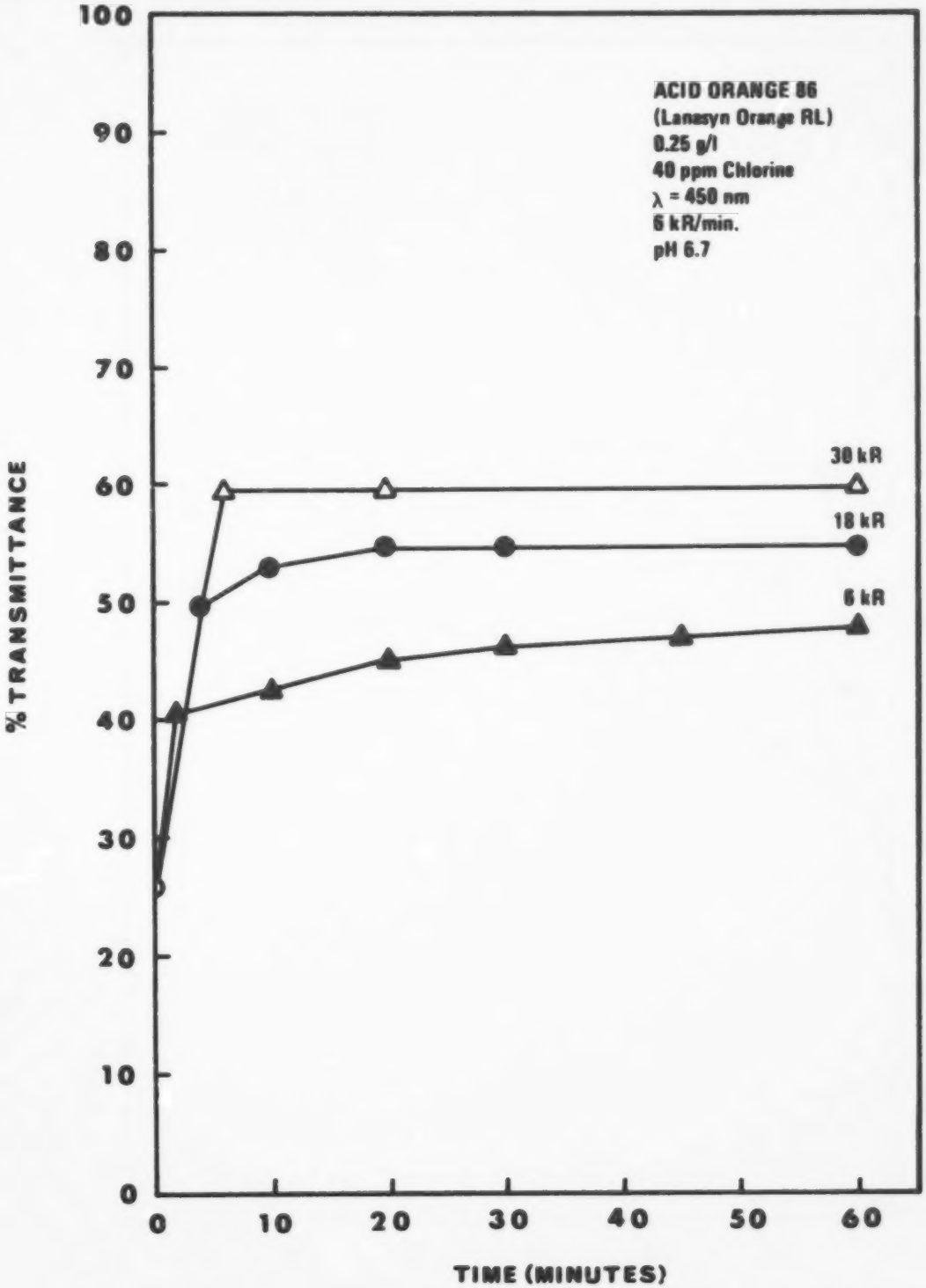

Figure 61 Transmittance Curves for Acid Orange 86 at pH 6.7 with 40 ppm Chlorine

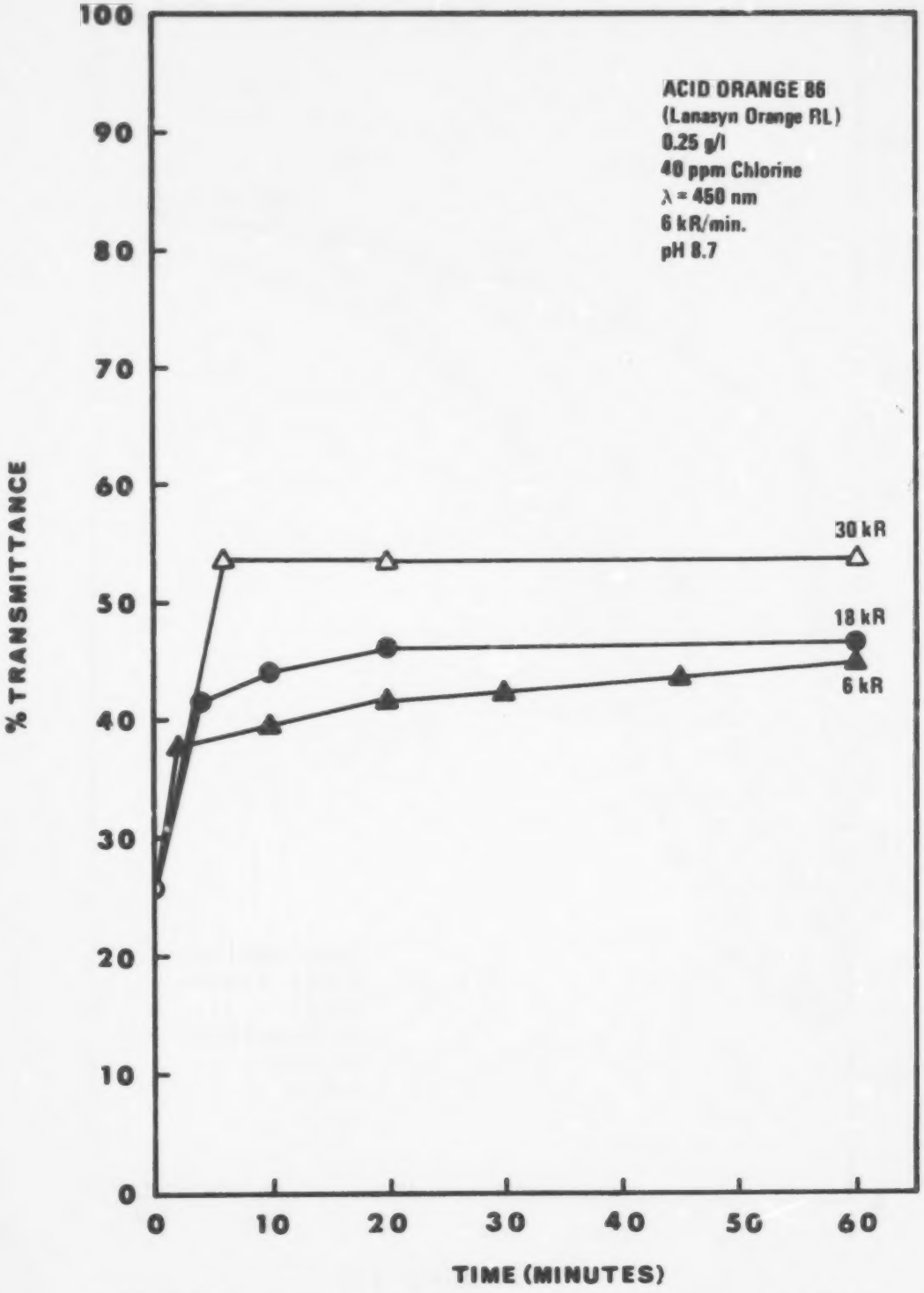

Figure 62 Transmittance Curves for Acid Orange 86 at pH 8.7 with 40 ppm Chlorine

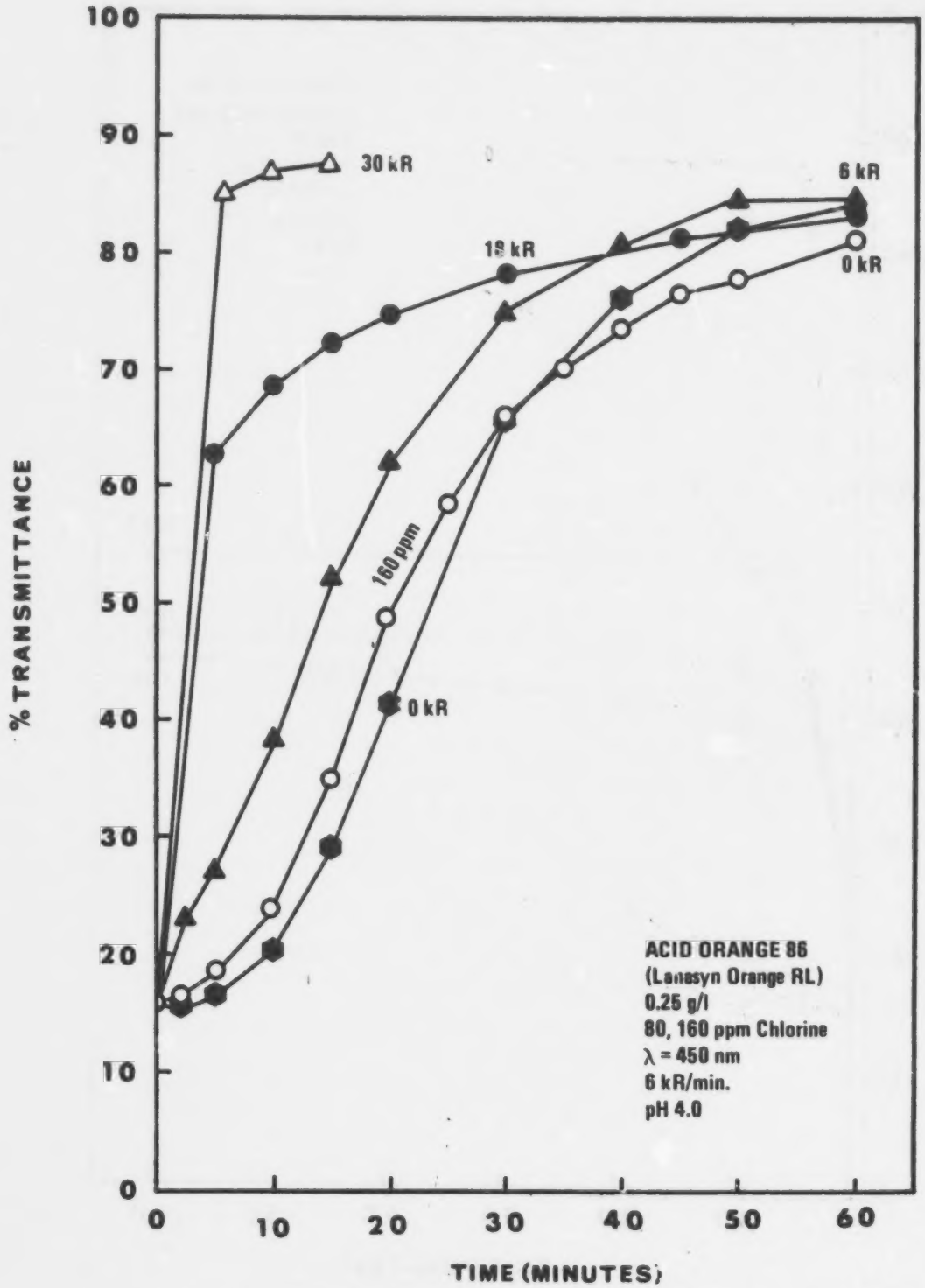

Figure 63 Transmittance Curves for Acid Orange 86 at pH 4.0 with 80 ppm Chlorine

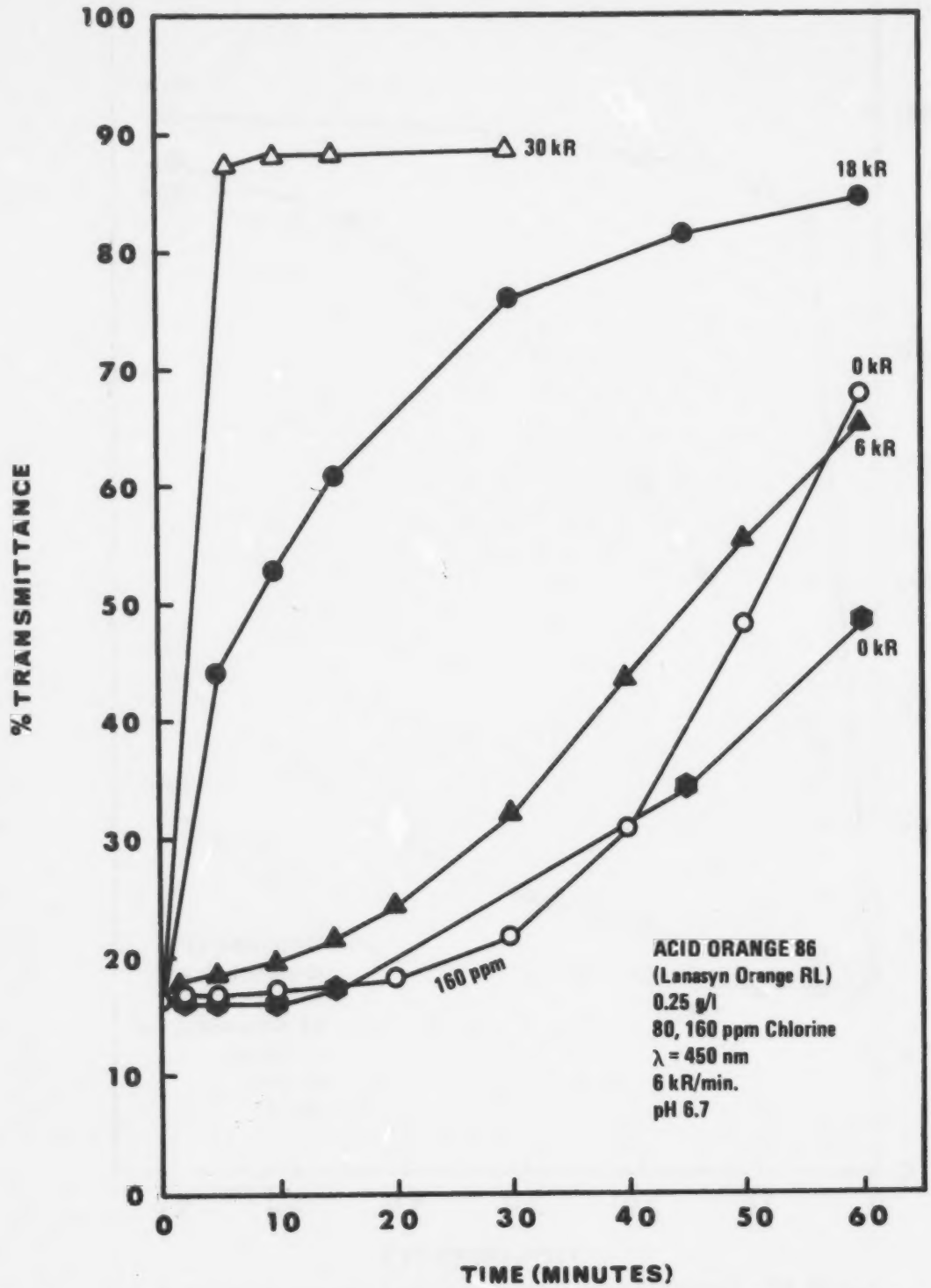

Figure 64 Transmittance Curves for Acid Orange 86 at pH 6.7 with 80 ppm Chlorine

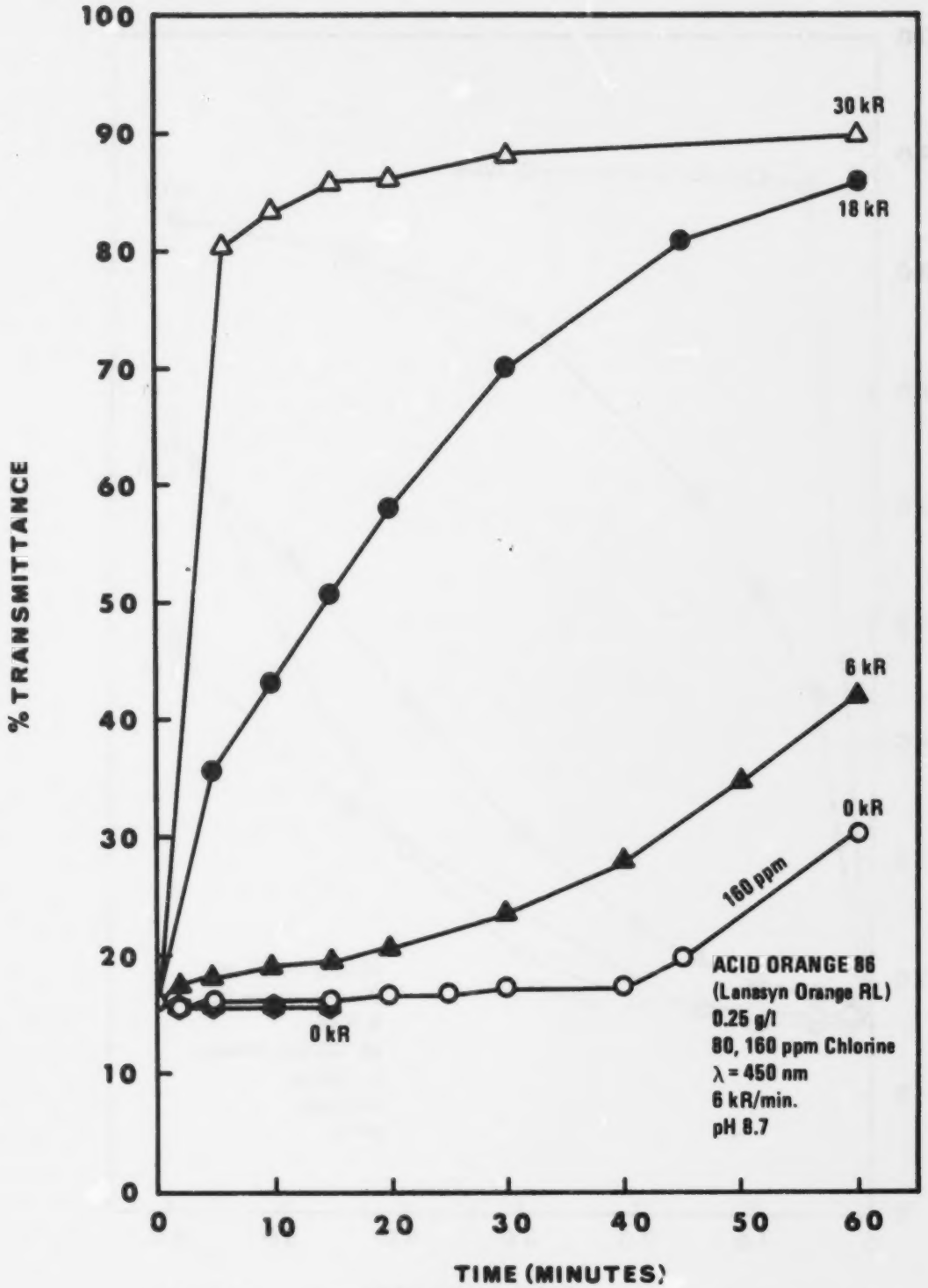

Figure 65 Transmittance Curves for Acid Orange 86 at pH 8.7 with 80 ppm Chlorine

SECTION VIII

APPENDIX

B. DESIGN STUDY FOR A REACTOR LOOP IRRADIATOR

I. Introduction

The Georgia Tech 12,000 curie cesium-137 gamma irradiator produces a uniform dose over a relatively small volume, and its usefulness is limited where large volumes require irradiation. The source configuration is such that an intense radiation field is available only at the bottom of a long well shielded 2" diameter tube, and it is very difficult to stir, make additions, or perform any other operation on a sample while it is actually in the irradiator.

Because of these mechanical limitations, consideration was given to the construction of a reactor loop irradiator facility (RLIF) in which a solution containing an appropriate element would be circulated through the Georgia Tech Research Reactor. Some of the element would become radioactive while passing through the flux region. The solution would then be passed through a coil outside the reactor where the gamma rays emitted by the decay of the radioactive element would be concentrated. This arrangement should provide a field of satisfactory volume, depending on the dimensions of the coil. The intensity of the field would then be determined by such matters as the nuclear properties of the chosen element, the capacity of the loop system, and the rate of flow.

The nuclear properties needed in the activable element include a large thermal neutron capture cross section, and the isotope produced should decay with energetic gamma emission and a short half-life to a short lived or stable daughter. It is important that no appreciable amount of long-lived activity be produced so that the facility can be shut down rapidly. The particular compound of the chosen element must be selected with consideration

of solubility, corrosiveness, and cost. These criteria limit severely the number of possible elements that could be used, and only aluminum, manganese, and silver were investigated.

A complete RLIF design would require a study of the theory of operation, material selection, shielding calculations, cost estimates, and preparation of engineering specifications. The present study was intended to determine answers to the fundamental questions concerning possible attainable field intensities and time to attain steady state conditions, for several potentially useable elements. A mathematical solution to the cyclic activation problem has been derived, and the usefulness of computer techniques in a parametric search for optimum operating conditions has been demonstrated.

This computer program can serve not only in a feasibility study of an RLIF, but can also be used to predict the resultant activity of any solute in conjunction with flow through a volume of approximately uniform neutron flux.

II. Theory

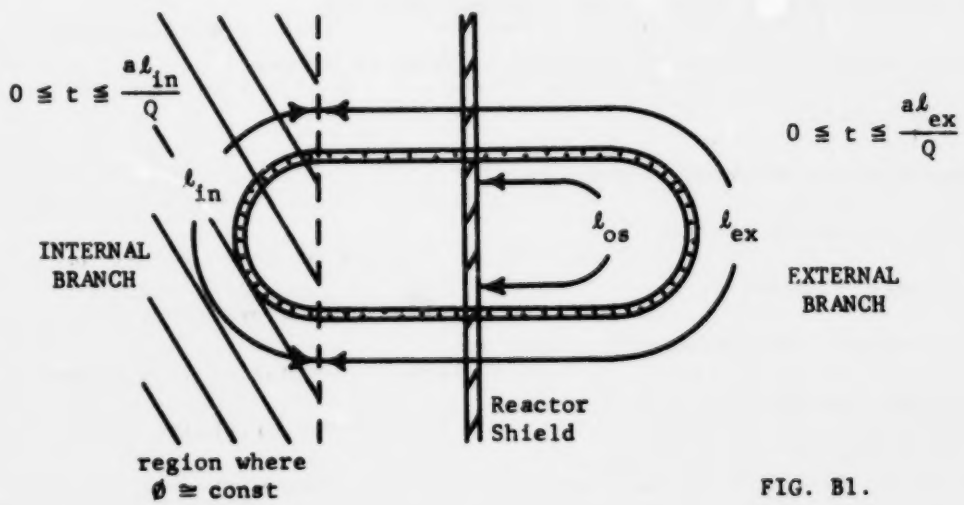

FIG. B1.

At any given time after the loop has been in operation, three types of nuclei will be present: (1) the original element, A^m, (2) the activated element, A^{m+1}, and (3) the decay product, B^{m+1}.

$$A^m + {}_0n^1 \rightarrow A^{m+1} \xrightarrow{\beta,\gamma} B^{m+1} \tag{B1}$$

By considering an arbitrarily small volume, ΔV, of the circulating fluid, and following its path throughout the loop, a solution to the problem can be approximated at any position of the k^{th} loop. The general equations governing the activity during any loop k at time t are:

$$\frac{dA_{in,k}}{dt} = -\lambda A_{in,k} + \left(\frac{\Delta V}{V} A_o n - A_{in,k} - B_k\right) \sigma\bar{\phi} \tag{B2}$$

$$\frac{dA_{ex,k}}{dt} = -\lambda A_{ex,k} \qquad k = 1,2,3,\ldots\text{cycles}$$

$A_{in,k}$ = number activated atoms in ΔV (internal branch)

$A_{ex,k}$ = number activated atoms in ΔV (external branch)

n = total number of moles of original element in system

λ = decay constant

B_k = number atoms of decay product in ΔV

V = total volume of system

A_o = Avogadro's number

σ = microscopic absorption cross section

$\bar{\phi}$ = average neutron flux

The buildup factor, B_k, was neglected since it is always small compared to the amount of original material present and results in an integral differential equation with no straightforward method of solution. After this approximation, the equations are solved simultaneously under the appropriate initial and boundary conditions, and an iterative solution is found that approaches a steady state value after a large number of cycles.

$$A_{in,k}(t) = \left[A_{ex,k-1}\left(\frac{a\ell_{ex}}{Q}\right) - \frac{\Delta V\ \Sigma_a\bar{\phi}}{\lambda+\sigma\bar{\phi}}\right] e^{-(\lambda+\sigma\bar{\phi})t} + \frac{\Delta V\ \Sigma_a\bar{\phi}}{\lambda+\sigma\bar{\phi}} \qquad (B3)$$

$$0 \leq t \leq \frac{a\ell_{in}}{Q}$$

$$A_{ex,k}(t) = A_{in,k}\left(\frac{a\ell_{in}}{Q}\right) e^{-\lambda t} \qquad 0 \leq t \leq \frac{a\ell_{ex}}{Q}$$

$$k = 1,2,3,\ldots\text{cycles}$$

Q = flow rate

a = cross sectional area of pipe

ℓ_{in} = pipe length internal

ℓ_{ex} = pipe length external

Σ_a = macroscopic absorption cross section

Such a solution is difficult to work with since the activity at any point depends on the solution to the previous branch of the loop. This necessitates a great deal of calculation to investigate each particular loop configuration.

III. Program

In order to vary parameters such as geometry, type and concentration of solute, and flow rate, a computer program was written that would facilitate rapid accumulation of the large quantity of data required. This program allows the user the option to change any of 12 input parameters and, for each set of input specifications, will perform a survey over a given array of element quantity (expressed in moles) and flow rates.

Briefly, the program operates as follows: Equations B3 are first used to determine the linear activity at the loop boundaries throughout the cycle. Hence, the solution can be found for any point and time by the reapplication of Eq. B3 with the appropriate boundary solution over the previous loop branch. The dose rate at the center of the irradiator coil is then estimated by calculating the contribution from each unit length of pipe in the coil at an effective radius from the center. This procedure is then repeated for the next cycle and is continued until the linear activity at a point in the k^{th} cycle differs by less than 0.1% with that in the k-1 cycle. When this condition is reached, the system is said to have reached steady state.

A complete history of the activation levels and radiation field strengths up to steady state is compiled by the computer and presented in tabular form in the output. AIN(I) and AEX(I) are the linear activity levels (in curies/cm) at the internal and external boundaries, respectively. TIME is the time in seconds and DOSE RATE gives the dose rate at the center of the coil in rad/hr. In addition, several other informative calculations are made after steady state is reached for purposes of comparison and later use. For example, the total activity in the pipe region external to the reactor is needed for use in shielding calculations.

INPUT CARD FORMATS

Card No.	Format	Use
1 2	80A1 80A1	First two cards contain 80 spaces each of alphanumeric information to be used as a problem heading.
3	I1,5X,I4	NN,NI NN is an integer optional output number. NN = 0 or 1. If NN = 0, the table of dose rate buildup is not printed and only the results after steady state are given. NI is the number of maximum iterations permitted if steady state is not reached. If exceeded, an internal error message is printed.
4 5	10E8.4	The 12 fixed input parameters are read in the order they appear under output heading. Two cards: 10 on first, 2 on second.
6+	E8.4	Any number of cards, less than 30, containing the values of the number of moles for element used in parametric survey. A negative number key card must be added at end.
37-67	E8.4	Same as cards 6-36 except the values are now for flow rates.

IV. Conclusions

1. Aluminum in the form of $Al(NO_3)_3 \cdot 6H_2O$ was found to be the most suitable of the elements investigated. In a system of 5000 cm^3 containing 9 moles of the material, a steady state dose rate of 1.73×10^3 rad/hr was indicated after 20.4 minutes. This represents 32.2% of the saturation activity and only 14.7 curies of activity outside the reactor.

In comparison, manganese in the form of $Mn(NO_3)_2 \cdot 6H_2O$ was capable of a higher dose rate in an identical facility, 7.05×10^4 rad/hr, but the steady state time was almost 430 minutes. This represents 24.1% of the saturation activity; however, with over 700 curies in the external branch at steady state, there would be definite shielding and safety problems.

$AgNO_3$ was investigated and found to give a high dose rate of almost 2×10^5 rad/hr, but appreciable buildup of the long-lived, 255 day, Ag^{110m} precludes the use of silver in an RLIF.

2. Except for activation products with half-lives less than about one minute, the flow rate is not a critical parameter. In general, the dose rate will be greater at the coil as the flow rate increases but there comes a point where a small increase in dose rate does not warrant additional pump size. For aluminum, $t_{\frac{1}{2}} = 2.27$ min, a flow rate of 1 gal/min is acceptable while for Ag^{107}, $t_{\frac{1}{2}} = 24.4$ sec, a rate of 4.5 gal/min brings the dose rate to within 80% of the maximum steady state dose rate.

3. The dose rate always increased as the number of moles increased.

The computer program follows this appendix and several pages of the printout for $Al(NO_3)_3$ are included for reference.

```
@SYSTEM$=ALTPRO.FORMB.IS IRRAD4
FOR 006-05/09-20:11 (:0)

    MAIN PROGRAM

00101    1*        DIMENSION O(30),N(30),ALP(160)                                  M001
00103    2*        REAL D,LIN,LEX,FL,SA,ML,E,MUR,VL,G,L,C1,C2,T,W,SAT,AC,AX,M,LOS,CD,  M002
        1CM,P,RF,N,V,C,MW,AIN1,AI#2,AEX1,AEX2                                    M003
00104    4*    92* FORMAT(8UA1)                                                    F001
00105    5*    92% FORMAT(10E8.4)                                                  F002
00106    6*    92E FORMAT('1'/1X,15X,80A1/'0',15X,80A1/3X,'D= ',E8.4,1X,'INCHES',16X,  F003
00106    7*       1'DIAMETER OF PIPE'/1X,'LIN= ',E8.4,1X,'INCHES',16X,'PIPE LENGTH WA  F004
00106    8*       2THIN FLUX REGION'/1X,'LEX= ',E8.4,1X,'INCHES',16X,'PIPE LENGTH EX:  F005
00106    9*       3ERNAL TO FLUX REGION'/1X,'LOS= ',E8.4,1X,'INCHES',16X,'PIPE LENGTH  F006
00106   10*       4 OUTSIDE REACTOR SHIELD'/2X,'FL= ',E8.4,1X,'NEUTS/(CM2*SEC)',7X,'M  F007
00106   11*       5VERAGE FLUX'/2X,'SA= ',E8.4,1X,'CM2',19X,'MICROSCOPIC ABSORPTION A  F008
00106   12*       6-SECT'/2X,'MW= ',E8.4,1X,'G/GMOLE',15X,'MOLECULAR WEIGHT'/2X,'ML=   F009
00106   13*       7',E8.4,1X,'SEC',19X,'HALF LIFE'/3X,'E= ',E8.4,1X,'MEV',19X,'GAMMA   F010
00106   14*       8ENERGY')                                                       FA10
00107   15*    927 FORMAT(1X,'MUR= ',E8.4,1X,'CM2/G',17X,'MASS-ABS COEF IN AIR'/2X,'L  F011
00107   16*       1D= ',E8.4,1X,'INCHES',19X,'COIL DIAMETER'/2X,'CM= ',E8.4,1X,'INCHE  F012
00107   17*       2S',16X,'COIL HEIGHT')                                          F013
00110   18*    928 FORMAT(E8.4)                                                    F014
00111   19*    929 FORMAT('0','SEQUENCE NUMBER (',I2,',',I2,')',5X,'FOR CALCULATIONS  F015
00111   20*       1WITH:'/'0',5UX,'(',I2,')',1X,'SOLUTE IN SYSTEM = ',E8.4,1X,'MOLES'  F016
00111   21*       2/5UX,'(',I2,')',8X,'FLOW RATE = ',E8.4,1X,'GAL/MIN')           F017
00112   22*    930 FORMAT('0',10X,'ITERATION I',7X,'AIN(I)',7X,'AEX(I)',9X,'TIME',4X,  F019
00112   23*       1'DOSE RATE'/47X,'I',9(5X,E8.4))                                F020
00113   24*    931 FORMAT(24X,I4,9(5X,E8.4))                                       F021
00114   25*    932 FORMAT('0','STEADY-STATE ACHIEVED AT TIME T = ',E8.4,1X,'MIN',2X,'  F022
00114   26*       1AFTER ',I4,1X,'CYCLES'/'0',25X,'CONCENTRATION',22X,' = ',E8.4,1X,'  F023
00114   27*       2GRAMS/LITER'/26X,'SATURATION ACTIVITY',17X,'= ',E8.4,1X,'CURIES/CM  F024
00114   28*       3'/26X,'MAX ACTIVITY AT EXIT OF FLUX REGION = ',E8.4,1X,'CURIES/CM'  F025
00114   29*       4/26X,'AVG ACTIVITY AT LOCATION OF COIL    = ',E8.4,1X,'CURIES/CM'/  F026
00114   30*       526X,'TOTAL ACTIVITY IN REGION'/31X,'EXTERNAL TO REACTOR SHIELD',5A  F027
00114   31*       6,'= ',E8.4,1X,'CURIES'/'0',25X,'CALCULATED DOSE RATE AT CENTER OF  F028
00114   32*       7COIL IS:',20A,'R = ',E8.4,1X,'RAD/HR',2X,51('0=0')/'0'/1X,120('*')/  FA28
00114   33*       81X,120('*'))                                                   F029
00115   34*    935 FORMAT(I1,5X,I4)                                                FC28
00116   35*    936 FORMAT('0',120('=')/'0',36X,'REFERENCE VOLUME = ',6X,E8.4,1X,'CM3'  F028
00116   36*       1/37X,'TOTAL VOLUME OF SYSTEM = ',E8.4,1X,'CM3'/37X,'DECAY CONSTANT  FE28
00116   37*       2 = ',8X,E8.4,1X,'SEC-1'/'0'/1X,'OPTION NUMBER = ',I1/'0'/1X,'MAX N  FF28
00116   38*       3UMBER OF ITERATIONS = ',I4/'0'/1X,120('*')/1X,120('*'))         FG28
00117   39*    936 FORMAT('0','***FAILURE TO CONVERGE***'/'0',25X,'CYCLES',10X,'= ',I  F029
00117   40*       14/26X,'TIME',16X,'= ',E8.4,1X,'MIN'/26X,'PRESENT ACTIVITY',6X,'= '  F030
00117   41*       2,E8.4,1X,'CURIES/CM'/26X,'SATURATION ACTIVITY = ',E8.4,1X,'CURIES/  F031
00117   42*       3CM'/'0'/1X,120('*')/1X,120('*'))                               F032
00120   43*       READ (5,926) (ALP(I),I=1,80),(ALP(I),I=81,160)                  H004
00132   44*       READ (5,935) MW,NI                                              HA04
00136   45*       READ (5,925) D,LIN,LEX,LOS,FL,SA,MW,ML,E,MUR,CD,CM              H005
00154   46*       WRITE (6,926) (ALP(I),I=1,80),(ALP(I),I=81,160),D,LIN,LEX,LOS,FL,S  H006
        1A,MW,ML,E                                                               H007
00177   48*       WRITE (6,927) MUR,CD,CM                                         H008
00204   49*       D=(2.540)*D                                                     H009
00205   50*       LIN=(2.540)*LIN                                                 H010
00206   51*       LEX=(2.540)*LEX                                                 H011
00207   52*       LOS=(2.540)*LOS                                                 H012
00210   53*       CD=(2.540)*CD                                                   H013
00211   54*       CM=(2.540)*CM                                                   H014
00212   55*       L=LIN+LEX                                                       H015
00213   56*       VL=(3.14159)*((D/2.)**2)                                        H016
00214   57*       VEVL*L                                                          HA16
00215   58*       G=ALOG(2.)/ML                                                   H017
00216   59*       WRITE (6,936) VL,V,G,MW,NI                                      HA17
00225   60*       DO 151 I=1,30                                                   H018
00230   61*       READ (5,928) N(I)                                               H019
00233   62*    151 IF (N(I).LT.0.) GO TO 152                                      H020
00236   63*    159 DO 153 I=1,30                                                  H021
00241   64*       READ (5,928) O(I)                                               H022
00244   65*    153 IF (O(I).LT.0.) GO TO 154                                      H023
00247   66*    154 DO 155 J=1,30                                                  H024
00252   67*        DO 156 I=1,30                                                  H025
00255   68*        IF (O(I).LT.0.) GO TO 155                                      H026
00257   69*        IF (N(J).LT.0.) STOP                                           H027
00261   70*        W=(80.3)*O(I)/(D**2)                                           H028
00262   71*        P=(7.66E+23)*N(J)/(L*D**2)                                     H030
```

Reproduced from best available copy.

```
00263   72*         AIN1=VL*P*SA*FL*(1.-EXP(-G*LIN/W))/(3.70E+10)                    M031
00264   73*         AEX1=AIN1*EXP(-G*LEX/W)                                          M032
00265   74*         RF=CC/9.*CD/(9.*COS(ATAN(CH/CD)))                                M033
00266   75*         WRITE (6,929) J,I,J,N(J),I,J,Q(I)                                M034
00276   76*         C=PW*N(J)*10.**3/V                                               M035
00277   77*         IF (NN.EQ.0) GO TO 158                                           M036
00301   78*         AC=AIN1*EXP(-G*LEX/(2.*W))                                       M037
00302   79*         R=(5.33E-05)*AC*E*CH*CD*MUR/(D*RF**2)                            M038
00303   80*         T=LIN/W*LEX/(2.*W)                                               M039
00304   81*         WRITE (6,930) AIN1,AEX1,T,R                                      M040
00312   82*   158 DO 147 K=2,N1                                                      M041
00315   83*         M=K-1                                                            M042
00316   84*         AIN2=AEX1*EXP(-G*LIN/W)+VL*(P/(3.70E+10)-AEX1/(G*VL))*SA*FL*(1.-EA  M043
00316   85*        1P(-G*LIN/W))                                                     M044
00317   86*         AEX2=AIN2*EXP(-G*LEX/W)                                          M045
00320   87*         C1=(AIN2-AIN1)/AIN2                                              M046
00321   88*         C2=(AEX2-AEX1)/AEX2                                              M047
00322   89*         IF (NN.EQ.0) GO TO 148                                           M048
00324   90*         T=M*L/W*LIN/W*LEX/(2.*W)                                         M049
00325   91*         AC=AIN2*EXP(-G*LEX/(2.*W))                                       M050
00326   92*         R=(5.33E+05)*AC*E*CH*CD*MUR/(D*RF**2)                            M051
00327   93*         WRITE (6,931) K,AIN2,AEX2,T,R                                    M052
00336   94*   148 AIN1=AIN2                                                          M053
00337   95*         AEX1=AEX2                                                        M054
00340   96*         IF (C1.LE..001.AND.C2.LE..001) GO TO 149                         M055
00342   97*   147 IF (K.EQ.N1) GO TO 150                                           M056
00345   98*   149 IF (NN.NE.0) GO TO 157                                           M057
00347   99*         T=M*L/W*LIN/W*LEX/(2.*W)                                         M058
00350  100*         AC=AIN1*EXP(-G*LEX/(2.*W))                                       M059
00351  101*         R=(5.33E+05)*AC*E*CH*CD*MUR/(D*RF**2)                            M060
00352  102*   157 T=T/60.                                                          M061
00353  103*         SAT=VL*P*SA*FL/(3.70E+10)                                        M062
00354  104*         AX=(1.*AIN1/G)*(EXP(-W*(LEX-LOS)/(2.*W))-EXP(-G*(LEX+LOS)/(2.*W)))  M063
00355  105*         WRITE (6,932) T,M,C,SAT,AIN1,AC,AX,R                             M064
00367  106*         IF ((M+1).NE.N1) GO TO 156                                       M065
00371  107*   150 M=M+1                                                            M066
00372  108*         T=(M*L/W*LIN/W*LEX/(2.*W))/60.                                   M067
00373  109*         SAT=VL*P*SA*FL/(3.70E+10)                                        M068
00376  110*         WRITE (6,934) K,T,AIN1,SAT                                       M069
00402  111*   156 CONTINUE                                                         M070
00404  112*   155 CONTINUE                                                         M071
00406  113*         STOP                                                             M072
00407  114*         END                                                              M073

      END OF COMPILATION:        NO  DIAGNOSTICS.
```

IRRAD4 -- AN IRRADIATION FACILITY DESIGN INCORPORATING AL(NO3)3*9H20

FIXED INPUT PARAMETERS

D=	.1000+01 INCHES	DIAMETER OF PIPE
LIN=	.1080+03 INCHES	PIPE LENGTH WITHIN FLUX REGION
LEX=	.2760+03 INCHES	PIPE LENGTH EXTERNAL TO FLUX REGION
LOS=	.1680+03 INCHES	PIPE LENGTH OUTSIDE REACTOR SHIELD
FL=	.3500+13 NEUTS/(CM2*SEC)	AVERAGE FLUX
SA=	.2340-24 CM2	MICROSCOPIC ABSORPTION X-SECT
MW=	.3752+03 G/GMOLE	MOLECULAR WEIGHT
HL=	.1362+03 SEC	HALF LIFE
E=	.1778+01 MEV	GAMMA ENERGY
MUR=	.4500-01 CM2/G	MASS-ABS COEF IN AIR
CD=	.6000+01 INCHES	COIL DIAMETER
CH=	.8000+01 INCHES	COIL HEIGHT

REFERENCE VOLUME = .5067+01 CM3
TOTAL VOLUME OF SYSTEM = .4942+04 CM3
DECAY CONSTANT = .5089-02 SEC-1

SEQUENCE NUMBER (1, 1) FOR CALCULATIONS WITH:

(1) SOLUTE IN SYSTEM = .5000+01 MOLES
(1) FLOW RATE = .2700+01 GAL/MIN

ITERATION I	AIN(I)	AEX(I)	TIME	DOSE RATE
1	.2778-02	.2498-02	.1859+02	.1327+03
2	.5174-02	.4653-02	.4762+02	.2471+03
3	.7242-02	.6512-02	.7664+02	.3459+03
4	.9025-02	.8116-02	.1057+03	.4311+03
5	.1056-01	.9500-02	.1347+03	.5046+03
6	.1189-01	.1069-01	.1637+03	.5680+03
7	.1304-01	.1172-01	.1927+03	.6227+03
8	.1402-01	.1261-01	.2218+03	.6698+03
9	.1488-01	.1338-01	.2508+03	.7105+03
10	.1561-01	.1404-01	.2798+03	.7457+03
11	.1625-01	.1461-01	.3088+03	.7759+03
12	.1679-01	.1510-01	.3379+03	.8021+03
13	.1726-01	.1553-01	.3669+03	.8246+03
14	.1767-01	.1589-01	.3959+03	.8441+03
15	.1802-01	.1621-01	.4249+03	.8609+03
16	.1833-01	.1648-01	.4539+03	.8753+03
17	.1859-01	.1672-01	.4830+03	.8878+03
18	.1881-01	.1692-01	.5120+03	.8986+03
19	.1901-01	.1709-01	.5410+03	.9079+03
20	.1918-01	.1724-01	.5700+03	.9159+03
21	.1932-01	.1737-01	.5991+03	.9228+03
22	.1944-01	.1749-01	.6281+03	.9288+03
23	.1955-01	.1758-01	.6571+03	.9339+03
24	.1965-01	.1767-01	.6861+03	.9384+03
25	.1973-01	.1774-01	.7152+03	.9422+03
26	.1979-01	.1780-01	.7442+03	.9455+03
27	.1985-01	.1785-01	.7732+03	.9483+03
28	.1991-01	.1790-01	.8022+03	.9508+03
29	.1995-01	.1794-01	.8313+03	.9529+03
30	.1999-01	.1798-01	.8603+03	.9548+03
31	.2002-01	.1801-01	.8893+03	.9563+03
32	.2005-01	.1803-01	.9183+03	.9577+03
33	.2008-01	.1805-01	.9474+03	.9589+03
34	.2010-01	.1807-01	.9764+03	.9599+03
35	.2011-01	.1809-01	.1005+04	.9608+03

STEADY-STATE ACHIEVED AT TIME T = .1676+02 MIN AFTER 35 CYCLES

CONCENTRATION	= .3796+03 GRAMS/LITER
SATURATION ACTIVITY	= .6827-01 CURIES/CM
MAX ACTIVITY AT EXIT OF FLUX REGION	= .2011-01 CURIES/CM
AVG ACTIVITY AT LOCATION OF COIL	= .1907-01 CURIES/CM
TOTAL ACTIVITY IN REGION EXTERNAL TO REACTOR SHIELD	= .8141+01 CURIES
DOSE RATE AT CENTER OF COIL	= .9608+03 RAD/HR *****

Reproduced from best available copy.

SEQUENCE NUMBER (1, 2) FOR CALCULATIONS WITH:

(1) SOLUTE IN SYSTEM = .5000+01 MOLES
(2) FLOW RATE = .8000+01 GAL/MIN

ITERATION I	AIN(I)	AEX(I)	TIME	DOSE RATE
1	.9505-03	.9170-03	.6275+01	.4702+02
2	.1855-02	.1789-02	.1607+02	.9176+02
3	.2715-02	.2619-02	.2587+02	.1343+03
4	.3533-02	.3409-02	.3566+02	.1748+03
5	.4312-02	.4160-02	.4546+02	.2133+03
6	.5053-02	.4875-02	.5525+02	.2500+03
7	.5758-02	.5555-02	.6505+02	.2848+03
8	.6428-02	.6202-02	.7484+02	.3180+03
9	.7066-02	.6817-02	.8464+02	.3496+03
10	.7673-02	.7403-02	.9443+02	.3796+03
11	.8250-02	.7960-02	.1042+03	.4082+03
12	.8799-02	.8490-02	.1140+03	.4353+03
13	.9322-02	.8994-02	.1238+03	.4612+03
14	.9819-02	.9473-02	.1336+03	.4858+03
15	.1029-01	.9930-02	.1434+03	.5092+03
16	.1074-01	.1036-01	.1532+03	.5314+03
17	.1117-01	.1078-01	.1630+03	.5526+03
18	.1158-01	.1117-01	.1728+03	.5728+03
19	.1196-01	.1154-01	.1826+03	.5919+03
20	.1233-01	.1190-01	.1924+03	.6102+03
21	.1268-01	.1224-01	.2022+03	.6275+03
22	.1302-01	.1256-01	.2120+03	.6440+03
23	.1334-01	.1287-01	.2218+03	.6597+03
24	.1364-01	.1316-01	.2316+03	.6747+03
25	.1392-01	.1343-01	.2414+03	.6889+03
26	.1420-01	.1370-01	.2512+03	.7024+03
27	.1446-01	.1395-01	.2610+03	.7153+03
28	.1471-01	.1419-01	.2708+03	.7275+03
29	.1494-01	.1441-01	.2805+03	.7392+03
30	.1516-01	.1463-01	.2903+03	.7502+03
31	.1538-01	.1484-01	.3001+03	.7608+03
32	.1558-01	.1503-01	.3099+03	.7708+03
33	.1577-01	.1522-01	.3197+03	.7804+03
34	.1596-01	.1539-01	.3295+03	.7894+03
35	.1613-01	.1556-01	.3393+03	.7981+03
36	.1630-01	.1572-01	.3491+03	.8063+03
37	.1645-01	.1588-01	.3589+03	.8141+03
38	.1661-01	.1602-01	.3687+03	.8215+03
39	.1675-01	.1616-01	.3785+03	.8286+03
40	.1688-01	.1629-01	.3883+03	.8353+03
41	.1701-01	.1641-01	.3981+03	.8417+03
42	.1714-01	.1653-01	.4079+03	.8478+03
43	.1725-01	.1665-01	.4177+03	.8536+03
44	.1737-01	.1675-01	.4275+03	.8591+03
45	.1747-01	.1686-01	.4373+03	.8644+03
46	.1757-01	.1695-01	.4471+03	.8694+03
47	.1767-01	.1705-01	.4569+03	.8741+03
48	.1776-01	.1713-01	.4567+03	.8786+03
49	.1785-01	.1722-01	.4765+03	.8829+03

50	.1793-01	.1730-01	.4863+03	.8870+03
51	.1801-01	.1737-01	.4961+03	.8909+03
52	.1808-01	.1745-01	.5058+03	.8946+03
53	.1815-01	.1751-01	.5156+03	.8981+03
54	.1822-01	.1758-01	.5254+03	.9015+03
55	.1829-01	.1764-01	.5352+03	.9047+03
56	.1835-01	.1770-01	.5450+03	.9077+03
57	.1840-01	.1776-01	.5548+03	.9106+03
58	.1846-01	.1781-01	.5646+03	.9133+03
59	.1851-01	.1786-01	.5744+03	.9159+03
60	.1856-01	.1791-01	.5842+03	.9184+03
61	.1861-01	.1796-01	.5940+03	.9208+03
62	.1866-01	.1800-01	.6038+03	.9230+03
63	.1870-01	.1804-01	.6136+03	.9251+03
64	.1874-01	.1808-01	.6234+03	.9272+03
65	.1878-01	.1812-01	.6332+03	.9291+03
66	.1882-01	.1815-01	.6430+03	.9310+03
67	.1885-01	.1819-01	.6528+03	.9327+03
68	.1889-01	.1822-01	.6626+03	.9344+03
69	.1892-01	.1825-01	.6724+03	.9360+03
70	.1895-01	.1828-01	.6822+03	.9375+03
71	.1898-01	.1831-01	.6920+03	.9389+03
72	.1901-01	.1834-01	.7018+03	.9403+03
73	.1903-01	.1836-01	.7116+03	.9416+03
74	.1906-01	.1839-01	.7213+03	.9428+03
75	.1908-01	.1841-01	.7311+03	.9440+03
76	.1910-01	.1843-01	.7409+03	.9451+03
77	.1912-01	.1845-01	.7507+03	.9462+03
78	.1914-01	.1847-01	.7605+03	.9472+03
79	.1916-01	.1849-01	.7703+03	.9481+03
80	.1918-01	.1851-01	.7801+03	.9491+03

STEADY-STATE ACHIEVED AT TIME T = .1300+02 MIN AFTER 80 CYCLES

CONCENTRATION	= .3796+03	GRAMS/LITER
SATURATION ACTIVITY	= .6827-01	CURIES/CM
MAX ACTIVITY AT EXIT OF FLUX REGION	= .1918-01	CURIES/CM
AVG ACTIVITY AT LOCATION OF COIL	= .1884-01	CURIES/CM
TOTAL ACTIVITY IN REGION EXTERNAL TO REACTOR SHIELD	= .8040+01	CURIES
DOSE RATE AT CENTER OF COIL	= .9491+03	RAD/HR ******

Reproduced from best available copy.

SEQUENCE NUMBER (2, 1) FOR CALCULATIONS WITH:

(2) SOLUTE IN SYSTEM = .9000+01 MOLES
(1) FLOW RATE = .2700+01 GAL/MIN

ITERATION I	AIN(I)	AEX(I)	TIME	DOSE RATE
1	.5000-02	.4497-02	.1859+02	.2388+03
2	.9314-02	.8376-02	.4762+02	.4449+03
3	.1303-01	.1172-01	.7664+02	.6226+03
4	.1625-01	.1461-01	.1057+03	.7759+03
5	.1901-01	.1710-01	.1347+03	.9082+03
6	.2140-01	.1925-01	.1637+03	.1022+04
7	.2346-01	.2110-01	.1927+03	.1121+04
8	.2524-01	.2270-01	.2218+03	.1206+04
9	.2678-01	.2408-01	.2508+03	.1279+04
10	.2810-01	.2527-01	.2798+03	.1342+04
11	.2924-01	.2630-01	.3088+03	.1397+04
12	.3023-01	.2718-01	.3379+03	.1444+04
13	.3108-01	.2795-01	.3669+03	.1484+04
14	.3181-01	.2860-01	.3959+03	.1519+04
15	.3244-01	.2917-01	.4249+03	.1550+04
16	.3299-01	.2966-01	.4539+03	.1576+04
17	.3346-01	.3009-01	.4830+03	.1598+04
18	.3386-01	.3045-01	.5120+03	.1617+04
19	.3421-01	.3077-01	.5410+03	.1634+04
20	.3452-01	.3104-01	.5700+03	.1649+04
21	.3478-01	.3127-01	.5991+03	.1661+04
22	.3500-01	.3148-01	.6281+03	.1672+04
23	.3519-01	.3165-01	.6571+03	.1681+04
24	.3536-01	.3180-01	.6861+03	.1689+04
25	.3551-01	.3193-01	.7152+03	.1696+04
26	.3563-01	.3204-01	.7442+03	.1702+04
27	.3574-01	.3214-01	.7732+03	.1707+04
28	.3583-01	.3222-01	.8022+03	.1711+04
29	.3591-01	.3229-01	.8313+03	.1715+04
30	.3598-01	.3236-01	.8603+03	.1719+04
31	.3604-01	.3241-01	.8893+03	.1721+04
32	.3609-01	.3246-01	.9183+03	.1724+04
33	.3614-01	.3250-01	.9474+03	.1726+04
34	.3617-01	.3253-01	.9764+03	.1728+04
35	.3621-01	.3256-01	.1005+04	.1729+04

STEADY-STATE ACHIEVED AT TIME T = .1676+02 MIN AFTER 35 CYCLES

CONCENTRATION	= .6833+03	GRAMS/LITER
SATURATION ACTIVITY	= .1229+00	CURIES/CM
MAX ACTIVITY AT EXIT OF FLUX REGION	= .3621-01	CURIES/CM
AVG ACTIVITY AT LOCATION OF COIL	= .3433-01	CURIES/CM
TOTAL ACTIVITY IN REGION EXTERNAL TO REACTOR SHIELD	= .1465+02	CURIES
DOSE RATE AT CENTER OF COIL	= .1729+04	RAD/HR ******

Reproduced from best available copy.

SEQUENCE NUMBER (2, 2) FOR CALCULATIONS WITH:

(2) SOLUTE IN SYSTEM = .9000+01 MOLES
(2) FLOW RATE = .8000+01 GAL/MIN

ITERATION I	AIN(I)	AEX(I)	TIME	DOSE RATE
1	.1711-02	.1651-02	.6275+01	.8464+02
2	.3338-02	.3221-02	.1607+02	.1652+03
3	.4887-02	.4715-02	.2587+02	.2418+03
4	.6360-02	.6136-02	.3566+02	.3147+03
5	.7762-02	.7488-02	.4546+02	.3840+03
6	.9095-02	.8775-02	.5525+02	.4500+03
7	.1036-01	.9999-02	.6505+02	.5127+03
8	.1157-01	.1116-01	.7484+02	.5724+03
9	.1272-01	.1227-01	.8464+02	.6292+03
10	.1381-01	.1332-01	.9443+02	.6833+03
11	.1485-01	.1433-01	.1042+03	.7347+03
12	.1584-01	.1528-01	.1140+03	.7836+03
13	.1678-01	.1619-01	.1238+03	.8301+03
14	.1767-01	.1705-01	.1336+03	.8744+03
15	.1853-01	.1787-01	.1434+03	.9165+03
16	.1934-01	.1865-01	.1532+03	.9566+03
17	.2011-01	.1940-01	.1630+03	.9947+03
18	.2084-01	.2011-01	.1728+03	.1031+04
19	.2154-01	.2078-01	.1826+03	.1066+04
20	.2220-01	.2142-01	.1924+03	.1098+04
21	.2283-01	.2203-01	.2022+03	.1130+04
22	.2343-01	.2261-01	.2120+03	.1159+04
23	.2400-01	.2316-01	.2218+03	.1188+04
24	.2455-01	.2368-01	.2316+03	.1214+04
25	.2506-01	.2418-01	.2414+03	.1240+04
26	.2556-01	.2466-01	.2512+03	.1264+04
27	.2602-01	.2511-01	.2610+03	.1288+04
28	.2647-01	.2554-01	.2708+03	.1310+04
29	.2689-01	.2595-01	.2805+03	.1331+04
30	.2730-01	.2634-01	.2903+03	.1350+04
31	.2768-01	.2671-01	.3001+03	.1369+04
32	.2804-01	.2706-01	.3099+03	.1387+04
33	.2839-01	.2739-01	.3197+03	.1405+04
34	.2872-01	.2771-01	.3295+03	.1421+04
35	.2904-01	.2801-01	.3393+03	.1437+04
36	.2933-01	.2830-01	.3491+03	.1451+04
37	.2962-01	.2858-01	.3589+03	.1465+04
38	.2989-01	.2884-01	.3687+03	.1479+04
39	.3015-01	.2909-01	.3785+03	.1491+04
40	.3039-01	.2932-01	.3883+03	.1504+04
41	.3062-01	.2955-01	.3981+03	.1515+04
42	.3085-01	.2976-01	.4079+03	.1526+04
43	.3106-01	.2996-01	.4177+03	.1537+04
44	.3126-01	.3016-01	.4275+03	.1546+04
45	.3145-01	.3034-01	.4373+03	.1556+04
46	.3163-01	.3052-01	.4471+03	.1565+04
47	.3180-01	.3068-01	.4569+03	.1573+04
48	.3197-01	.3084-01	.4667+03	.1582+04
49	.3212-01	.3099-01	.4765+03	.1589+04

50	.3227-01	.3114-01	.4863+03	.1597+04
51	.3241-01	.3127-01	.4961+03	.1604+04
52	.3255-01	.3140-01	.5058+03	.1610+04
53	.3268-01	.3153-01	.5156+03	.1617+04
54	.3280-01	.3164-01	.5254+03	.1623+04
55	.3291-01	.3176-01	.5352+03	.1628+04
56	.3302-01	.3186-01	.5450+03	.1634+04
57	.3313-01	.3196-01	.5548+03	.1639+04
58	.3323-01	.3206-01	.5646+03	.1644+04
59	.3332-01	.3215-01	.5744+03	.1649+04
60	.3341-01	.3224-01	.5842+03	.1653+04
61	.3350-01	.3232-01	.5940+03	.1657+04
62	.3358-01	.3240-01	.6038+03	.1661+04
63	.3366-01	.3247-01	.6136+03	.1665+04
64	.3373-01	.3255-01	.6234+03	.1669+04
65	.3380-01	.3261-01	.6332+03	.1672+04
66	.3387-01	.3268-01	.6430+03	.1676+04
67	.3393-01	.3274-01	.6528+03	.1679+04
68	.3400-01	.3280-01	.6626+03	.1682+04
69	.3405-01	.3285-01	.6724+03	.1685+04
70	.3411-01	.3291-01	.6822+03	.1687+04
71	.3416-01	.3296-01	.6920+03	.1690+04
72	.3421-01	.3301-01	.7018+03	.1692+04
73	.3426-01	.3305-01	.7116+03	.1695+04
74	.3430-01	.3309-01	.7213+03	.1697+04
75	.3434-01	.3314-01	.7311+03	.1699+04
76	.3439-01	.3317-01	.7409+03	.1701+04
77	.3442-01	.3321-01	.7507+03	.1703+04
78	.3446-01	.3325-01	.7605+03	.1705+04
79	.3450-01	.3328-01	.7703+03	.1707+04
80	.3453-01	.3331-01	.7801+03	.1708+04

STEADY-STATE ACHIEVED AT TIME T = .1300+02 MIN AFTER 80 CYCLES

CONCENTRATION = .6833+03 GRAMS/LITER
SATURATION ACTIVITY = .1229+00 CURIES/CM
MAX ACTIVITY AT EXIT OF FLUX REGION = .3453-01 CURIES/CM
AVG ACTIVITY AT LOCATION OF COIL = .3392-01 CURIES/CM
TOTAL ACTIVITY IN REGION
EXTERNAL TO REACTOR SHIELD = .1447+02 CURIES

DOSE RATE AT CENTER OF COIL = .1708+04 RAD/HR ******

Reproduced from best available copy.

*U.S. GOVERNMENT PRINTING OFFICE 1973 514-154/255 1-3